

ELECTRODEPOSITED INORGANIC SEPARATORS

FINAL REPORT

Ву

W.N. Carson Jr., and J.A. Consiglio

August 1966

Prepared for

GODDARD SPACE FLIGHT CENTER
NATIONAL AERONAUTICS
AND SPACE ADMINISTRATION
GREENBELT, MARYLAND

CONTRACT NAS 5-9168



S-66-1019

FOREWORD

This final report on work performed under Contract NAS 5-9168 summarizes the program devoted to the evaluation of calcium and magnesium hydroxide films for use as separators in silver-cadmium cells. The work was sponsored by the Goddard Space Flight Center in Greenbelt, Maryland.

The work was conducted at the General Electric Company's Research and Development Center in Schenectady, New York. Dr. J. A. Consiglio was the project engineer. Dr. W. N. Carson provided technical guidance in planning the experimental program and in interpretation of experimental results. Mr. E. L. Roberts performed most of the experimental work.

TABLE OF CONTENTS

Section		Page
1	SUMMARY	1
2	INTRODUCTION	3
	Coating Process Description	3 4
3	TECHNICAL DISCUSSION	7
	Experimental Procedures and Equipment Coating Parameter Study Results Electrode Performance Studies	7 12 31 43
4	NEW TECHNOLOGY STATEMENT	53
5	RECOMMENDATIONS	55
	APPENDIX I Magnesium Hydroxide Film Data	
	APPENDIX II Calcium Hydroxide Film Data	
	APPENDIX III Calcium Hydroxide Film Data	
	APPENDIX IV Electrolyte Concentration Study Data	
	APPENDIX V Electrode Polarization and Cell Potential Data	
	APPENDIX VI Data for Electrodes Used in Modified YS-5 A.H. Cells	

LIST OF ILLUSTRATIONS

Figure		Page
1	Schematic Diagram of Electrode Coating Apparatus .	8
2	Magnesium Hydroxide Films on Discharged Silver Plates	14
3	Calcium Hydroxide Films on Discharged Silver Plates .	15
4	Calcium Hydroxide Films on Discharged Silver Plates .	16
5	Calcium Hydroxide Films on Discharged Silver Plates.	17
6	Calcium Hydroxide Films on Discharged Silver Plates .	18
7	Calcium Acetate Coated Silver Electrodes	2 5
8	Effect of Variables on Film Thickness Uniformity (Intermediate Level of Electrolyte Agitation)	28
9	Effect of Variables on Film Thickness Uniformity (Intermediate Level of Electrolyte Agitation)	29
10	Effect of Variables on Film Thickness Uniformity (High Level of Electrolyte Agitation)	30
11	Test Cell Components	33
12	Test Cell Assembly	34
13	Discharge Voltage Curves 5 A.H. Cells	3 6
14	Typical Polarization Curve for Calcium Hydroxide Coated Electrode	39
15	Calcium Hydroxide Coated Electrodes After Cycling Tests	41
16	Nylon Separator Wrapped Around Calcium Hydroxide Coated Electrode After Cycling	42
17	Calcium Hydroxide Coated Silver Electrodes for Modified 5 A. H. Cells Electrodes Used in Cell Number 1	49
18	Calcium Hydroxide Coated Silver Electrodes for Modified 5 A.H. Cells Electrodes Used in Cell Number 10	50
19	Partially Assembled Modified 5 A.H. Cell	51

LIST OF TABLES

Table		Page
1	Film Deposition Parameters	12
2	Effect of Electrode State and Pretreatment on Calcium Hydroxide Films	23
3	Effect of Electrolyte Concentration and Electrode State of Charge on Film Quality	26
4	Preferred Process Parameter Values for Calcium Hydroxide Films	31
5	Capacity Data for Calcium Hydroxide Coated Silver Electrodes	35
6	Polarization Data for Coated Silver Electrodes	37
7	Comparison of Silver Transported Through Calcium Hydroxide Films	40
8	Effect of Sterilization on Capacity	. 44
9	Effect of Sterilization on Polarization	45
10	Comparison of Cell Resistance with Electrode Film Thickness and Sterilization History	46
11	Cycled Electrode Results	47

Section 1

SUMMARY

The objective of this program was the evaluation of thin electrodeposited films of calcium and magnesium hydroxides for use as separators in silver-cadmium cells. Potential gains to be achieved with these separators are increased thermal stability at elevated temperatures and a reduction in silver migration with lower overall separator thickness requirements.

The work program was conducted in two phases. The first phase consisted of an investigation to determine the effect of process parameters on the resulting film properties.

The parameters investigated were electrolyte type, concentration, current density and electrode substrate condition with respect to state of charge and liquid content. The principal film characteristics determined as a function of the above parameters were film weight, film thickness and density, and changes in resistance attributed to the film. In addition to these quantitative film characteristics, film adherence and uniformity of coverage of the electrode were determined on a qualitative basis.

The second phase of the work was concerned with evaluating the performance of the coated electrodes in terms of capacity developed under short term charge-discharge cycling, polarization increases contributed by electrodes with films of varying thickness, and control of silver transport. In addition, the effect of sterilization at 145°C on the above performance criteria was evaluated.

The process parameter studies showed that the calcium hydroxide films on silver electrodes were more adherent and uniform in electrode coverage than the magnesium hydroxide films. For the calcium hydroxide films, the preferred process parameter ranges for obtaining adherent film thicknesses of one to five mils per side are: electrolyte concentrations of 70 to 280 grams per liter of calcium acetate buffered with one to two grams per liter of calcium hydroxide using current densities of 75 to 150 milliamperes per square centimeter. Film adherence was improved by depositing films on silver electrodes which had previously been cycled once and discharged and which contained no liquid in the pores prior to immersion in the coating bath. Film weight and thickness were found to correlate as a linear function of the ampere-hour product. The coulombic efficiency in the preferred process variable range approached 50 percent. The film densities based on photomicrographic examination and calculations from weight gain and thickness determinations are in the range of 85 to 100 percent of the theoretical calcium hydroxide density. The resistance increases caused by the film as measured by a 1000 cycles per second bridge did not correlate strongly with film thickness, weight increase or ampere-hour product.

The performance evaluation studies showed that the coated electrodes developed their nominal capacity after short term, constant current charge and discharge cyclic tests (six to twelve cycles). Polarization measurements on coated silver electrodes showed no large increases as a function of film thickness or when compared to uncoated electrodes at discharge rates equivalent to a one C rate. At 0.1 ampere (~0.1 C rate) coated electrode polarization values ranged from 4 to 13 percent lower than the average of uncoated electrodes. At 1.0 ampere (~1.0 C rate) the polarization values ranged from 10 percent lower to 20 percent greater than the average for the uncoated electrodes.

The films are effective in controlling silver transport based on analysis made after a short number of cycles (six to twelve). The silver transported through the films and collected on a nylon separator ranged from 13 to 55 percent of the amounts collected for uncoated electrodes. The sterilization studies showed that the coated electrodes could be heated to 145°C for a period of 40 hours in either degassed 31 percent by weight potassium-hydroxide solution or in nitrogen without the loss of the coating. The performance of these electrodes in subsequent cell tests with respect to capacity, polarization and silver transport was similar to that obtained with unsterilized coated electrodes.

Ten five-ampere-hour silver-cadmium cells were modified and will be tested by Goddard Space Flight Center personnel for longer term performance evaluation. Five of these cells contain silver electrodes coated with calcium hydroxide of a nominal film thickness of two mils, and five cells have a nominal film thickness of five mils.

Section 2

INTRODUCTION

This report summarizes the research and development work performed under Contract NAS 5-9168. The work program was aimed at evaluating thin, electrodeposited films of calcium and magnesium hydroxide for use as separators in silver-cadmium cells. The principal potential advantages to be gained from the successful development of these separators are an increase in chemical stability of the cell separators at elevated temperature and a reduction in silver migration.

The objective of the program was twofold: first, to determine the effect of process parameters on film thickness and porosity, film resistance, and adherence of the films on representative silver and cadmium electrodes; second, to evaluate the performance of these films in single silver electrode cells in terms of capacity developed, internal cell resistance, increase in polarization characteristics, control of silver transport, and stability at elevated temperatures.

Prior to this contract, the General Electric Company had been investigating the feasibility of using thin films of electrodeposited calcium and magnesium hydroxide as separators, mainly in nickel-cadmium cells. Some exploratory experiments with these films on silver electrodes showed significant reductions of silver transport from the electrode to the electrolyte phase during extended periods of charge and overcharge and also during prolonged periods of discharge (3 months) at low discharge rates (1-10 milliamperes) in silver-zinc cells. The ability of these films to prevent or reduce silver migration during cyclic operation had not been tested and was one of the areas to be investigated under this contract. In addition, the films deposited on commercially available silver electrodes increased the internal resistance of the test cells by factors of 10 to 20, compared to uncoated electrodes. This resistance increase is related to the porosity and pore size of the electrode structure, the extent to which the pores are filled with film, and the total thickness and porosity of the film. It was therefore necessary to determine the film deposition process conditions, which minimized the resistance increase, and at the same time formed films of adequate structural integrity.

COATING PROCESS DESCRIPTION

The films are deposited directly on the surfaces of the battery plates by making the plate the cathode in an electrolysis cell, using soluble salts of calcium or magnesium as the electrolyte. Although, theoretically, any soluble calcium or magnesium salt may be used, the nitrate and acetate have been found to give the most desirable results.

The mechanism of the electrodeposition process involves the discharge of hydrogen gas at the cathode via the following reaction:

$$2H_2O + 2e \rightarrow H_2 + 2OH$$

As the electrolysis proceeds and hydrogen gas is evolved, the local concentration of hydroxyl ion at the cathode-electrolyte interface becomes high enough to exceed the solubility product of calcium or magnesium hydroxide, and precipitation of the hydroxide takes place on the surface of the cathode. With the use of an inert anode, such as stainless steel in combination with an aqueous solution of calcium acetate, the overall reaction is:

$$Ca (C_2H_3O_2)_2 + 3H_2O \rightarrow Ca (OH)_2 + 2HC_2H_3O_2 + H_2 + 1/2O_2$$

The oxygen is evolved at the anode and results from the oxidation of water at its surface

$$2H_2O \rightarrow O_2 + 4H^+ + 4e$$

Since acetic acid is produced in the reaction, which tends after a period of time to make the solution unduly acid, solid calcium hydroxide powder may be added prior to or during the electrolysis. Such additions serve not only to keep the pH of the electrolyte constant but also to keep the concentration of calcium acetate constant. The solid calcium hydroxide will react with the acetic acid according to the following reaction:

$$Ca (OH)_2 + 2HC_2H_3O_2 \rightarrow Ca (C_2H_3O_2)_2 + 2H_2O$$

The overall reactions which occur when using magnesium acetate, magnesium nitrate and calcium nitrate are:

1. Mg
$$(C_2H_3O_2)_2 + 3H_2O \rightarrow Mg (OH)_2 + 2HC_2H_3O_2 + H_2 + 1/2O_2$$

2. Mg
$$(NO_3)_2 + 3H_2O \rightarrow Mg(OH)_2 + 2HNO_3 + H_2 + 1/20_2$$

3. Ca
$$(No_3)_2 + 3H_2O \rightarrow Ca (OH)_2 + 2HNO_3 + H_2 + 1/20_2$$

Of course, in Equations 1 and 2, magnesium hydroxide will be deposited and magnesium oxide or hydroxide powder should be added to the electrolysis cell to neutralize the hydrogen ion released at the anode.

The above reactions apply to the process when using fully discharged electrodes. In the case of fully charged positive electrodes, the coating process tends to discharge the electrode with the production of hydroxyl ions. These in turn will cause precipitation of calcium or magnesium hydroxide without the evolution of hydrogen.

PROGRAM SCOPE

It was proposed to conduct the work in three phases:

Phase I -- Coating Process Parameter Studies

Phase II -- Electrode Performance Studies

Phase III -- Cadmium Electrode Studies

The work to be done in each phase is outlined below.

Phase I -- Coating Process Parameter Studies

The objective of these studies was to determine the effect of the deposition process parameters and electrode surface condition on the resulting film properties. The process parameters investigated were electrolyte type, calcium and magnesium acetate, electrolyte concentration, current density, and electrode substrate condition. Commercially available silver electrodes were to be used.

The film characteristics which were determined were weight, thickness, uniformity, composition, and resistance in potassium hydroxide solutions as a function of deposition conditions and thickness. The stability of the films at temperatures of 145°C was also investigated.

Phase II -- Electrode Performance Studies

The objective of these studies was to evaluate the performance of coated electrodes in comparison to uncoated electrodes. The principal characteristics examined were electrode capacity, polarization, and internal cell resistance for varying coating thicknesses. Also, the amount of silver transported through the films after short term cycling tests was examined.

The effect of sterilizing coated and uncoated electrodes at 145°C for a period of forty hours on the above performance characteristics was also investigated.

Phase III -- Cadmium Electrode Studies

Work in this area was contingent upon examining the results from test cells containing only coated silver electrodes. If these results indicated that a suitable minimum electrode-separator resistance could not be readily obtained, then cadmium electrodes would be coated and evaluated. The results obtained in test cells containing coated silver electrodes were sufficiently promising and therefore no work was done with cadmium electrodes.

Section 3

TECHNICAL DISCUSSION

EXPERIMENTAL PROCEDURES AND EQUIPMENT

The experimental procedures and equipment used in the various phases of the program are described in this section. These will be treated under four categories: coating process, electrodes, film characteristics, and electrode performance characteristics.

Coating Process

The coating of electrodes was done in an experimental setup shown schematically in Figure 1. The electrolyte (approximately one liter) bath was contained in a two liter beaker mounted on a variable speed magnetic stirrer -- Will Corporation Model 252300. The electrode to be coated was immersed in the bath and was centered between two planar counter electrodes made of stainless steel screen. The screens were approximately three inches square. Separation between the electrode being coated and the counter electrodes was approximately one inch. Connection to the electrode being coated was made with an alligator clip. To obtain high coulombic efficiency and assist in obtaining uniform coating of the electrode, it was necessary to insulate connecting electrical leads penetrating the electrolyte. Electrolyte pH and calcium or magnesium ion concentration were controlled by periodic addition of one gram quantities of the hydroxides of calcium or magnesium. Chemicals used in the makeup of the electrolytes and other solutions in the program were certified reagent grade purchased from the Fisher Scientific Company.

A coating run was made at a constant current controlled by the direct-current power supply -- Harrison Laboratories Model 808A. The coating time was monitored with a stop watch. During the coating process, the voltage rise was monitored. This served as a rough guide to coating thickness build-up.

Electrodes

The silver electrodes used in the program were obtained from commercially available cells. Three types of electrodes were used:

Electrodes from "Silcad" cells Yardney Model YS5-(S)-4. These plates have a nominal capacity of one and one-quarter ampere-hour. The plate dimensions are approximately 1-1/2 inches by 1-5/8 inches, 28-29 mils thickness, and weigh 6.5 to 7.0 grams in the discharged state.

Electrodes from "Silcad" cells Yardney Model YS5. These plates have a nominal capacity of one ampere-hour. The plate dimensions are 1-7/16 inches by 1-3/4 inches, 22-23 mils thickness and weigh 4.7 to 4.9 grams in the discharged state.

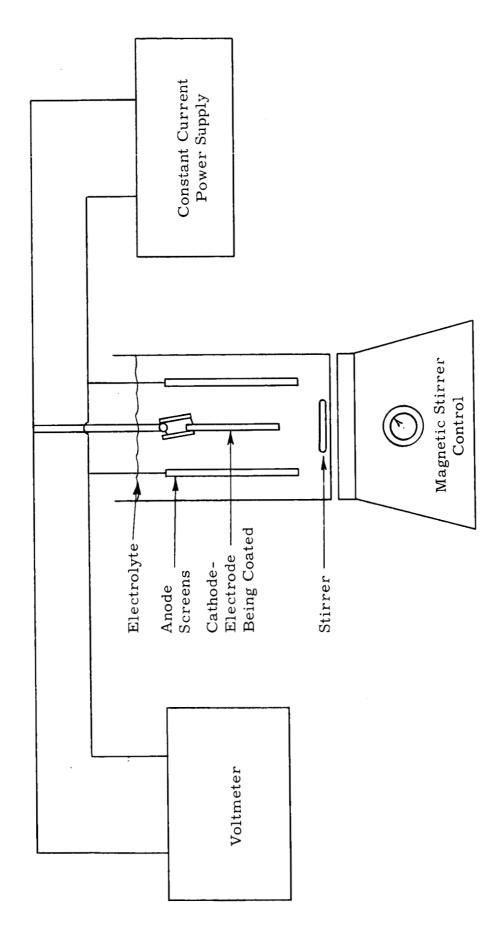


Figure 1. Schematic of Electrode Coating Apparatus.

Electrodes from Electric Storage Battery Company used in the Mariner Satellite cells. These plates were cut down to a sample size of 1-7/16 inches by 1-3/4 inches, 20-21 mils thickness and weigh 4.0 to 4.3 grams. The nominal capacity of the plates is 0.33 ampere-hour per gram of active material. The screen grid weight is 0.2 gram per square inch of electrode area.

During the course of the work, electrodes were pretreated to determine the effect on coating uniformity, adherence and resistance increase. The pretreatments were of two kinds -- one with respect to the state of charge of the electrode and the other with respect to the presence or absence of electrolytes within the porous electrode structure prior to deposition of the film on the electrode. The state of charge of the electrodes prior to coating were as follows:

- 1. Uncharged as removed from the commercial cells.
- 2. Cycled-discharged, cycled once, charged at 200 milliamperes for five hours for plates of one ampere-hour nominal capacity and for six hours for 1.2 ampere-hours nominal capacity plates. The discharge was at 250 milliamperes for four and five hours respectively for the two plate capacities and then shorted to the cadmium counter electrode overnight.
- 3. Cycled-charged, cycled once as described above (2) and then charged again at 200 milliamperes for five and six hours respectively for the two nominal capacities.
- 4. Reverse Coated, electrodes of types (1) and (2) above, were partially charged in the coating electrolyte for a period of ten to twenty minutes prior to reversing the polarity and then proceeding with the deposition of the hydroxide.

The electrodes in one of the above conditions were pretreated by one of the following steps prior to immersion and coating in the electrolyte. The designations used in the report to identify these pretreatments and descriptions of the treatments are as follows:

- 1. Potassium Hydroxide -- the electrode was soaked in a 31 percent by weight solution of potassium hydroxide for a period of twenty-four hours, removed from the solution, and the excess solution was sponged off with a paper towel.
- 2. Water -- the electrode was first soaked as described in Item 1 above, then rinsed in distilled water until the water rinse was essentially neutral, removed from the water, and excess water was sponged off with a paper towel.
- 3. Dried -- the electrode was treated as described in Item 2 and then was dried in an air-circulating oven at 145°C for a period of two hours.

Film Characteristics

The primary film characteristics determined in the course of the program were film weight, film thickness, and resistance increase. These characteristics were determined as a function of electrolyte type and concentration, current density, and coating time.

Film weight was determined by weighing the electrode before and after coating; generally, the electrode was in the discharged state. The electrode was dried in an oven at 145°C for at least one hour prior to making the weight measurement.

Film thickness was determined from micrometer measurements that were made on the electrode before and after coating. The values reported are the differences of the average of at least five measurements made on each electrode before and after coating. The measurements were made at the four corners of the electrode and in the center.

Resistance increase contributed by the film was determined with a 1000 cycles per second bridge -- General Radio Model 1650A. The procedure was to measure the resistance of the electrode against an inert electrode, in a cell containing 31 percent by weight solution of potassium hydroxide at electrode separation increments of 0.5, 1.0, and 1.5 inches. These resistance values were extrapolated to zero separation to obtain the effective resistance of the electrode-electrolyte interface. The resistance gain values reported are the difference between extrapolated values before and after coating.

In addition to these quantitative characteristics, electrodes were examined visually for completeness of coverage after coating. The adherence of the coating was evaluated qualitatively by hand-rubbing the coating in the dried state with a paper towel. For the more adherent films, this rubbing process resulted in the removal of a small amount of powdery hydroxide from the surface of the coating. A more quantitative index of the adherence of the films emerged from observations made while making 1000 cycles per second resistance measurements on the coated electrodes. Poorly adhering films generally sloughed off the electrodes during the soaking of the electrode in distilled water or in the 31 percent by weight solution of potassium hydroxide prior to making the resistance measurements.

Film porosity was not determined by direct measurements. Approximate calculations based on the weight gain and film thickness for the thicker films showed that the film density approaches the theoretical density of the hydroxide. Photomicrographic examination of sectioned coated electrodes at magnifications up to 750 X showed no discernible pore structure.

Electrode Performance Characteristics

The primary performance characteristics tested for the coated electrodes were capacity and polarization. The capacity was determined by short term

cyclic charge and complete discharge at a constant current (6 to 12 cycles). These tests were conducted in open flooded test cells containing one coated electrode between two sintered matrix type cadmium counter electrodes. The electrolyte was 31 percent by weight solution of potassium hydroxide. In the first test cells the electrodes were assembled without any separator between electrodes. Subsequent testing showed that shorts would develop in the course of the cycling, primarily at the edges where in many cases the electrodes were not completely coated. Later test cells employed one or two layers of nylon separator (approximately 10 mils in thickness) wrapped around the coated silver electrode and an open mesh plastic grid between the wrapped electrode and the cadmium counter electrodes. Cell potential was recorded during charge and discharge on Rustrak recorders.

Individual silver electrode potential was measured against a mercury-mercuric oxide reference electrode. The reference electrode fitted into a well that was connected to the cell electrolyte by a 1/16-inch diameter hole at the bottom of the test cell. The polarization of the silver electrode was determined at various discharge currents up to one ampere (approximately one C rate).

The effectiveness of the films in reducing silver transport was determined by analyzing the nylon separator and in some cases the cell electrolyte for silver content. For the separator, the analytical method employed was to add excess ammonium hydroxide to complex the silver. The solution was boiled and taken to dryness. Water was added, the nylon separator was removed, and the solution acidified with 30 percent by weight nitric acid. The silver was precipitated with sodium chloride, filtered, washed, dried, and weighed. The results are reported in milligrams of silver chloride. Comparative tests were made with uncoated electrodes.

The effect of sterilizing the coated silver electrodes at 145°C was also investigated. The procedure was varied, since problems with the electrodes showing low capacity after sterilizing developed in the course of the work. The procedure used in the early tests consisted of immersing the electrodes in a solution of 31 percent by weight potassium hydroxide contained in a Teflon beaker. The Teflon beaker in turn was set into a steel bomb and sealed. The sample was then heated in an oven at 145°C for a period of 40 hours.

Later sterilizations were conducted in two modes. One mode, designated as <u>Dry</u>, consisted of placing the electrodes in the beaker and bomb assembly, flushing the system for 5 to 10 minutes with dry nitrogen, and then sealing the bomb. The sample was then heated as described above. The second mode was designated as <u>Wet</u>, and the potassium-hydroxide solution was first degassed by boiling for approximately fifteen minutes. The balance of the precedure was as described above.

COATING PARAMETER STUDY RESULTS

The deposition process variables and electrode states, as well as the value range of the variables investigated, are summarized in Table 1. The sequence in which the effect of variables on film characteristics were investigated is outlined below and is followed by a discussion of the results and conclusions.

Table 1 FILM DEPOSITION PARAMETERS

Value

Electrochemical

Current Density 5 - 155 ma/cm²
Time 5 - 165 minutes

Electrolyte Concentration 70 - 350 g/l calcium acetate

20 - 450 g/l magnesium acetate

Hydroxide Buffer
Concentration

0 - 1 g/1

Electrode State

Uncharged as-received condition

Cycled-discharged charged @ 200 ma for 6 hours discharged @ 250 ma for 5 hours for 1. 2 ampere-hour plates and

shorted overnight

Cycled-charged as above, then recharged @

200 ma for 6 hours for 1.2

ampere-hour plates

Reverse Coated charged in coating electrolyte for

10 to 20 minutes prior to coating

Pore Content 1. 31% potassium hydroxide

2. 1 plus distilled water rinse

3. $1+2 + dried @ 145^{\circ}C$ in air

In the first part of the study, the objective was to determine the relative merits of calcium hydroxide films versus magnesium hydroxide films. This was then followed by a more detailed study of the variables for the calcium hydroxide films, since the magnesium hydroxide films were found to be inferior to the calcium hydroxide films.

The exploratory runs to compare calcium hydroxide films versus magnesium hydroxide films were made over a range of electrolyte concentrations with and without excess solid hydroxide present in the electrolyte bath. In each case the silver electrodes were coated over a range of current densities

varying the coating time at each current density to determine the range of film weight, film thickness, and increase in resistance contributed by the film. A given electrode was coated at fixed current density and fixed time. For the majority of these runs the electrodes were in the uncharged and dry state prior to immersion into the electrolyte for coating. A few runs were made with electrodes cycled once in the discharged state as described previously. During the course of these runs, there were variations in the speed of the magnetic stirrer used to agitate the electrolyte. Furthermore, the method of holding the electrode in the bath was varied in an effort to minimize stray currents.

Exploratory Deposition Studies

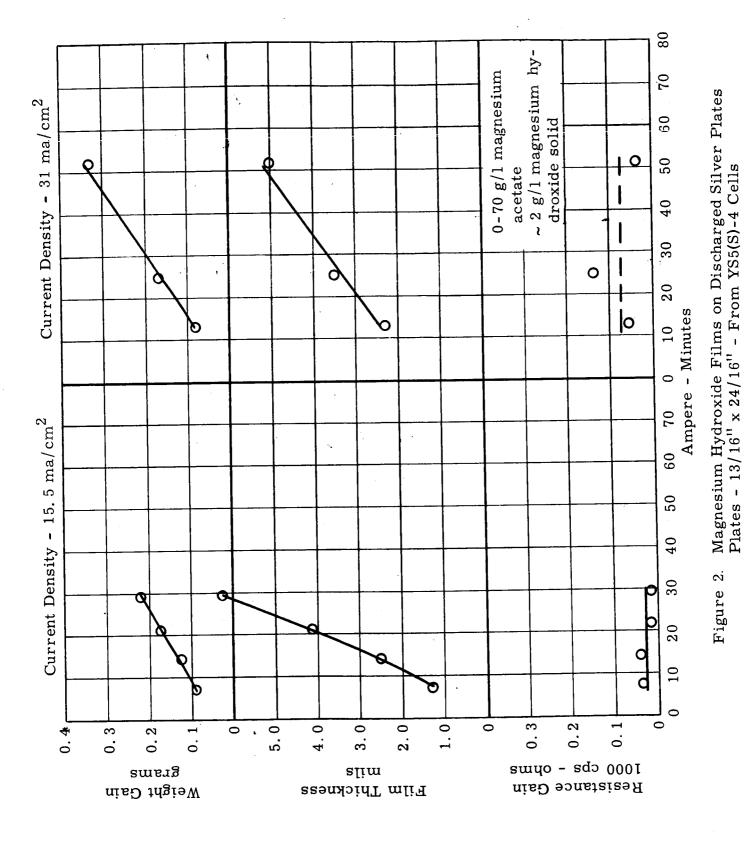
The experimental data including process variable values and film characteristic values for these tests are recorded in Appendices I and II for magnesium hydroxide and calcium hydroxide films respectively.

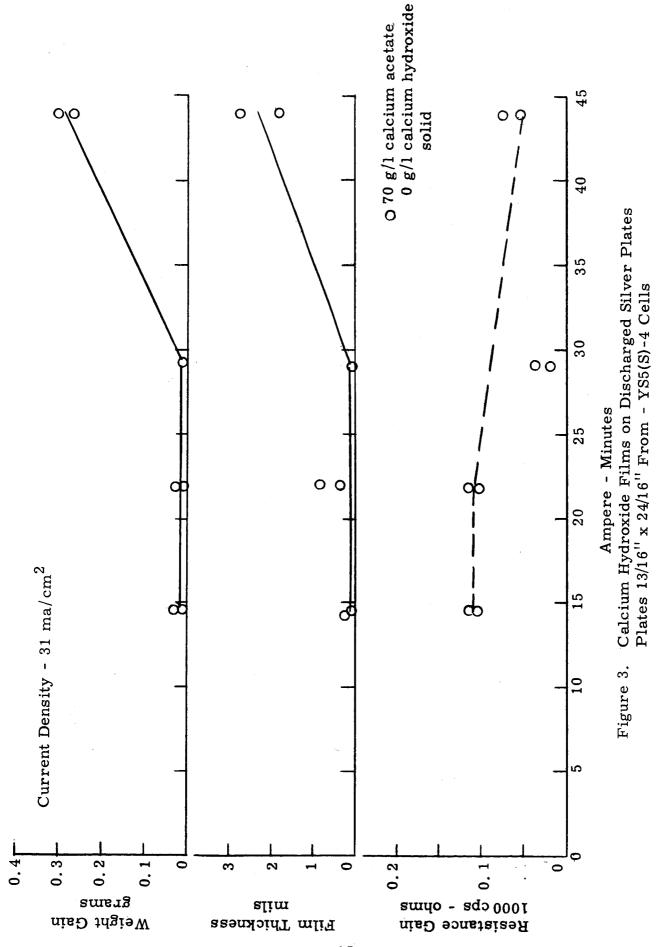
For the magnesium hydroxide films, the range of electrolyte concentration was from 20 to 450 grams per liter of magnesium acetate saturated with magnesium hydroxide. The current density range was from 3.9 to 46.5 milliamperes per centimeter squared. Coating times ranged from 30 to 120 minutes, with the majority of the runs being made at 30 to 60 minutes. The electrodes used were taken from YS 5-(S)-4 cells. Sample electrodes used were either one-half the original dimensions or uncut as removed from the cells.

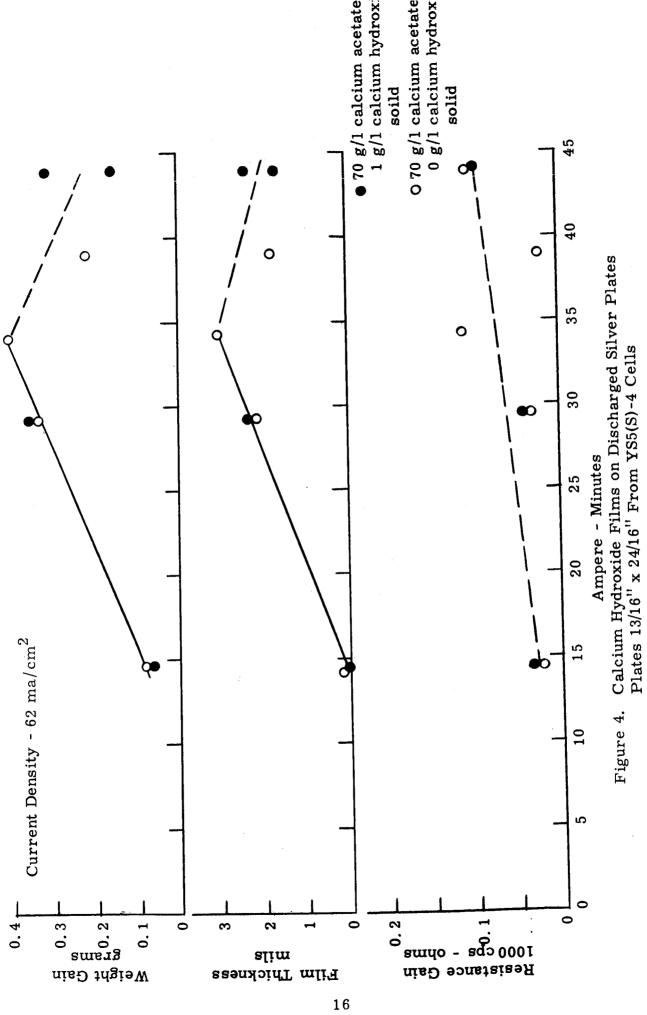
For the calcium hydroxide films the electrolyte concentration was held constant at 70 grams per liter of calcium acetate saturated with calcium hydroxide. The current density range was from approximately 15 milliamperes per centimeter squared to 155 milliamperes per centimeter squared. Coating time ranged from 5 to 165 minutes.

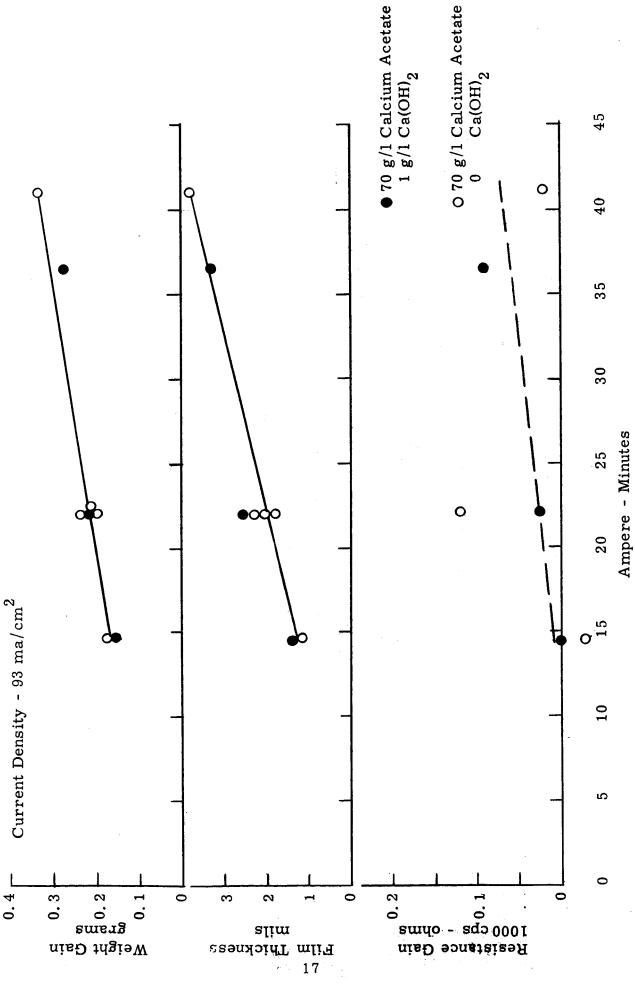
Film Characteristics -- The total film weight, film thickness, and the resistance increase data were examined for correlation with the ampereminute product. Typical data, shown in Figures 2 through 6, illustrate the relationship between these film characteristics and the ampereminute product for the range of current densities investigated.

Film weight and film thickness obtained from a given electrolyte concentration were found to be linear functions of the number of coulombs transferred. Coulombic efficiency correlation with current density was not noted on the basis of data in hand. The coulombic efficiency for the calcium hydroxide films deposited from an electrolyte concentration of 70 grams per liter, ranged from approximately 25 to 50 percent over the current density range of 31 to 155 milliamperes per centimeter squared. For the more adherent magnesium hydroxide films, the coulombic efficiency ranged from approximately 30 to 60 percent. The corresponding ranges of electrolyte concentration and current densities for these tests were 20 to 450 grams per liter and 15.5 to 31 milliamperes per centimeter squared respectively.

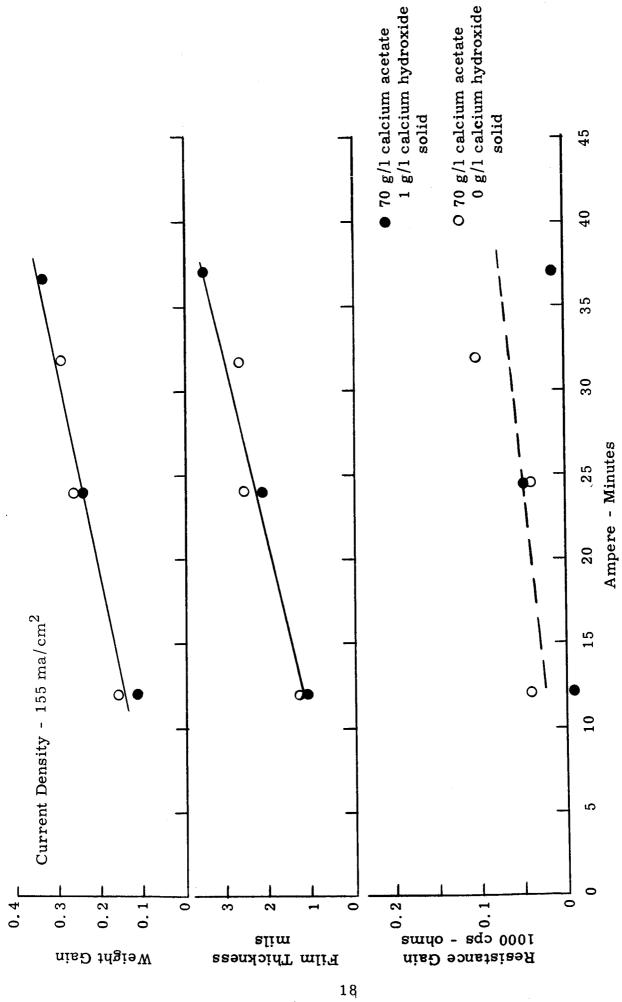








Calcium Hydroxide Films on Discharged Silver Plates: Plates - 13/16" x 24/16" -From YS5(S)-4 Cells. Figure 5.



Calcium Hydroxide Films on Discharged Silver Plates Plates - 13/16" x 24/16" - From YS5(S)-4 Cells Figure 6.

Resistance increase values for the films in general showed a greater degree of scatter and poorer correlation with ampere-minute product than either the film weight or film thickness data. Some of the factors which contributed to this are discussed more fully in the following text.

Some of the more qualitative film characteristics such as adherence and uniformity of coverage, other observations, and general conclusions from these exploratory runs are summarized below:

1. Adherence and Uniformity of Coverage

The adherence and uniformity of coverage of the magnesium hydroxide films to the electrode structure were generally poor, compared to the calcium hydroxide films. The most adherent and more uniform magnesium hydroxide films were obtained when excess solid magnesium hydroxide was present in the electrolyte bath (greater than 1 to 2 grams per liter) or at the highest electrolyte concentration examined (450 grams per liter of magnesium acetate). Practically all of the magnesium hydroxide films sloughed off to varying degrees when immersed in distilled water, or 31 percent by weight potassium hydroxide solution. In some instances a very thin (thickness not measured) insulating film remained on the electrode after the outer portion of the film had sloughed off. The calcium hydroxide in general did not slough off, and coverage, although not complete in many cases, was definitely superior to the magnesium hydroxide films. As a rule the films build up from the bottom edge of the electrode toward the top. Coverage was poorest in the area of the electrical connection to the electrode and around the edges. Longer coating times tended to improve the overall coverage. In the next phase of the work, insulation of all electrical leads penetrating into the electrolyte and an increase in rotational speed of the stirrer in the bath improved the coverage and uniformity of the film.

2. Other Observations and General Conclusions

Film thickness for the calcium hydroxide case of 4 to 5 mils per side could be achieved with sufficient coating time at most of the current density values tested. In most cases, for the magnesium hydroxide, the ability to form films of comparable thicknesses was not possible, except for the concentration level previously noted. Evidence that a significant film thickness was being achieved during a run could be detected by the gradual increase in voltage across the cell. For the thicker calcium hydroxide films (three to five mils per side) the voltage rise was approximately forty volts. For the magnesium hydroxide films the voltage increase observed in all runs was less than one volt. This was the case even when appreciable film thicknesses (greater than one mil per side) were obtained. The factor or factors contributing to this difference in coatability were not resolved during the course of the work.

It is believed that the lower solubility of the magnesium hydroxide is the most significant factor in the difference of ability to coat the electrodes and the adherence after coating.

It is postulated that for successful buildup of an adhering film on the electrode the following conditions must be satisfied. The hydroxyl ions must be formed and retained in a thin boundary layer adjacent to the porous metal electrode substrate. Initial precipitations must take place within the porous substrate by diffusion of cations into the boundary layer. If precipitation takes place in a zone removed from the metal-liquid interface, then the solid phase formed is dispersed into the bulk of the liquid phase. The latter process occurs in all runs to some degree, due to the gross agitation of the solution by the magnetic stirring as well as localized agitation created by the release of hydrogen from the electrode. Thus, for a given set of operative conditions, such as current density value (i.e., hydroxyl ion generation rate) and localized turbulence level, the lower the solubility of the reaction product the greater will be the tendency for precipitation to occur further away from the metalliquid interface. Lowering the rate of hydroxyl ion generation, while maintaining a high cation concentration, should help to overcome this tendency. Attempts in this direction were made by reducing the current density values for magnesium coatings down to 3.9 milliamperes per centimeter squared (one-quarter of the lowest value used for the calcium hydroxide films). The results were not encouraging since film thicknesses were barely measurable. From a practical processing point of view, it did not appear promising to reduce the current density values still further, since the processing time to obtain films of several mils would be too long. It is conceivable that differing crystal structures of the solid phase precipitate, possible changes in state of hydration of the films, and accompanying volume changes with varying pH could influence adherence and the ability to build up film thickness. Time prohibited an investigation of sufficient detail to establish the validity of these speculations. It is believed that the argument presented above is most consistent with all of the observations, particularly the lack of voltage rise in the case where a film buildup was obtained. Additional evidence in support of this point is presented in the following pages.

Resistance increase values, compared to the film weight and film thickness values, showed the highest degree of scatter and lowest level of correlation with ampere-hour input. This was due in part to the variation in resistance values observed for uncoated silver electrodes. An initial check of a number of uncoated (i.e., as received) electrodes yielded extrapolated resistance values ranging from 0.07 to 0.21 ohm for one-half size plates. Subsequent tests with full size electrodes showed that extended soaking of the electrodes for periods greater than twenty-four hours increased the penetration of electrolyte into the pores of the electrode. Under these

conditions the resistance values of uncoated full-size electrodes ranged from 0.08 to 0.17 ohm. The increased soaking reduced the maximum to minimum value ratio to approximately two to one from three to one.

On the basis of these results and considerations previously discussed, it was decided to continue the process variables study for calcium hydroxide films, followed by the evaluation of performance of those films that appeared most promising.

Calcium Hydroxide Deposition Studies

Following the exploratory tests, emphasis was placed on delineating more accurately the range of process variable values yielding coatings with improved overall characteristics. Additional deposition tests were made over a range of concentrations, similar to that done for the magnesium hydroxide films. The electrode substrate condition was varied with respect to state of charge, and the effect of the absence or presence of electrolyte within the pores was also investigated. More attention was devoted to determining qualitatively the effect of increasing solution agitation rate. Finally, additional experimentation was made with insulation of leads penetrating the electrolyte bath to reduce stray current flow.

The primary objective was to determine if adherence and uniformity of coverage could be improved, and if resistance increase values could be made more reproducible and lower in value than observed in the exploratory runs. From the exploratory studies previously discussed, it appeared that the most uniform coatings and reproducible results were obtained in the current density range between 62 and 155 milliamperes per centimeter squared. On the basis of these studies it was decided to first investigate the effect of several electrode state and pretreatment combinations at a fixed electrolyte concentration and current density. This study was followed by an investigation of electrolyte concentration using two of the more promising electrode state-pretreatment combinations as a parameter.

Concurrent with this phase of the work, the evaluation of the performance characteristics of some of the better electrodes was started. The results of the latter are discussed in the next section.

Electrode State and Pretreatment Study Results -- For these tests full size electrodes (i. e., 1-5/8 by 1-1/2 inches) that were removed from Yardney Model YS 5-(S)-4 cells were used. The electrodes were all coated in one liter of electrolyte, containing 70 grams per liter of calcium acetate buffered with approximately 1.0 gram of calcium hydroxide. Additional calcium hydroxide was added in 1.0 gram increments after every two to three coating runs. The current density for all runs was 93 milliamperes per centimeter squared. The coating time was normally 20 minutes, with a few experiments at 15 and 30 minutes.

Following the coating step, the electrodes were rinsed with distilled water, soaked in potassium hydroxide for a period of twenty-four hours and the 1000 cycles per second resistance measurements were made. The electrodes were rinsed again in distilled water, oven dried at 145°C for one hour, weighed and remeasured for thickness.

The experimental and calculated data for this set of experiments are recorded in Appendix III. A condensed tabulation of the film characteristics and general film quality versus the various combinations of electrode state and pretreatment is given in Table 2. The term "Reverse Coating" in Table 2 indicates that the electrode was first charged in the coating electrolyte bath for the period of time indicated, and then the polarity was reversed to start the film deposition process. The electrode pretreatment prior to the reverse coating was in the dried condition as described previously in this section under "Electrodes."

The most significant conclusions drawn from an examination of the data recorded in Table 2 are as follows:

- 1. The electrodes, regardless of state charge, which contained no liquid in the pores and were dried, produced the most uniform and complete films. The electrodes containing water in the pores were intermediate in this respect, and poor films or no films were achieved with potassium hydroxide in the pores.
- 2. The electrodes which had been cycled and discharged or charged produced the most uniform and complete films. Visually, the films produced from the charged electrodes were more uniform in appearance than the cycled and discharged electrodes.
- 3. Resistance increases continued to be variable. Resistance values of pretreated coated electrodes showed less increase than had been observed in the previously discussed exploratory experiments.

The lack of significant film thickness buildup for the electrodes containing potassium hydroxide or water in the pores is additional supporting evidence that effective film growth requires a thin boundary layer at the metalelectrolyte interface. This layer must have a high concentration of cations available at the interface.

Under the conditions of liquid purposely left in the pores, the zone of precipitation was extended to the outer surface of the electrode and most of the precipitate went into the bulk of the solution. An examination of the voltage increase across the cell obtained at the end of the coating runs, showed voltage increases for the electrodes having no coatings or partial coatings ranging from 12 to 35 volts. This voltage increase across the cell is in marked contrast to the one volt increase obtained in all of the runs attempted with magnesium hydroxide.

TABLE 2

EFFECT OF ELECTRODE STATE AND PRETREATMENT
ON CALCIUM HYDROXIDE FILMS

Electrode-State and Pretreatment		No.	Resista ohm <u>Initial</u>		Weight Gain Grams	Film Thickness mils/side	Remarks on Film Quality
Uncharged-KOH		3 4 8 12	.150 .150 .111	.080 .043 .101	.073 .068 .034 .043	0.1 <0.1 <0.1 0.1	Partially Coated No Coat No Coat No Coat
Reverse for 10	Coating min.	2	.111 .080	.062 .127	.045	1.4	Coated
H ₂ O		6 7 15 16	.112 .112 .092 .111	.083 .053 .112 .088	.105 .100 .032 .037	0.4 0.4 <0.1	Partially Coated Partially Coated No Coat No Coat
Dried		10 11	.100 .120	.110 .090	.178 .191	0.85 1.05	Coated Coated
Cycled-Discharged	-кон	5 9	.043 .098	.100 .061	0.200 0.164	2.25 2.55	Partially Coated Partially Coated
	н ₂ о	1 13	.110 .081	.068 .119	.324 .437	3.0 3.2	Coated Coated
	Reverse Coating for 20 min.	19 20* 17*	.162 .100 .130	.072 .260 .060	362 +.371 075	0 4.7 1.9(1)	No Coat Coated Partially Coated (1)Thickness where coated
	Dried	21 22	.170 .170	0.080 0.070	.254 .288	1.5 1.5	Coated Coated
Charged-H ₂ O		23 24 14	.140 .130 .120	.130 .300 .070	.480 .718 .295	1.4 3.0 1.8(1)	Coated Coated Partially Coated (1)Thickness where coated
Dried .		18 25	.170 .170	.175 .175	.304 .525	1.25 2.0	Coated Coated

NOTES: Electrodes - Full Size Silver 1-5/8" x 1-1/2" Electrolyte Concentration - 70 g/1 of calcium acetate Coating Time - 20 minutes nominal Current Density - $93~\text{ma/cm}^2$

^{*}Coated in a fresh volume of electrolyte after reversal.

These observations support the overall thesis that to form adhering films and achieve subsequent film thickness increase, the initial film deposition must occur within the porous electrode structure. Presumably, this growth of film in the pores forms an interlocking network with the metallic substrate and determines, in large part, the extent of film adherence. The nature of the initial film formation and the mechanism whereby it continues to grow cannot be conclusively deduced from the experimental results in hand. Since the calcium hydroxide is an insulator, and not known to be an ionic conductor, these results suggest that the transport of hydroxyl ions through the film depends on a fine pore structure containing a liquid phase in which the hydroxyl ions are transported. One point that is difficult to resolve is the observed large voltage drop that develops while the film is deposited and the low value of effective resistance displayed by the coated electrodes when used as a battery electrode. This point is discussed in more detail in Section 4,"Electrode Performance Studies."

The persistent scatter and poor reproducibility of resistance gain values is probably also related to the structure of the initial film deposited. An additional factor is the pore structure of the electrode substrate which would control the extent of penetration by the electrolyte and the amount of electrolyte held in the electrode and, consequently, the amount of film formed in the pores. Detailed investigations of these factors were beyond the scope of the current program.

A random check of the density of the thicker films calculated from the weight gain and thickness measurements show values ranging from 85 to 100 percent of the theoretical value for the calcium hydroxide films. Crosssectional photomicrographs of the films at a magnification of 645X also show a relatively dense structure compared to electrode substrate structure. Figure 7 illustrates this observation.

Electrolyte Concentration Study Results -- In this phase of the process parameter studies, the effect of electrolyte concentration on film characteristics was investigated. The concentration levels used were 140, 280, and 360 grams per liter of calcium acetate. The two most promising electrode states, as determined from previous studies, were cycled-discharged and cycled-charged. These states were used as parameters for this study. Subsequent to the adjustment of the state of charge, the electrodes were thoroughly rinsed in distilled water and dried at 145°C in air for one hour. The current density was held constant at 93 milliamperes per centimeter squared. The coating time was varied to obtain film thickness over the range of 1 to 5 mils per side.

Electrodes of the three types discussed previously were used in the tests. The experimental and calculated data for these tests are recorded in Appendix IV. A condensed tabulation of the data is given in Table 3. An analysis of these data shows the following significant effects:

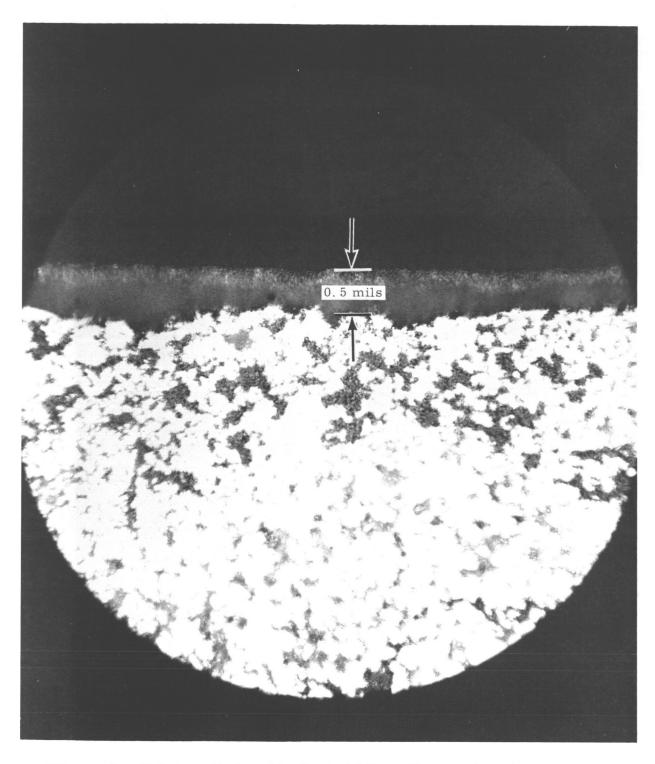


Figure 7. Calcium Hydroxide Coated Silver Electrodes; As-polished; Bright Field Illumination, 645X.

Table 3

EFFECT OF ELECTROLYTE CONCENTRATION AND ELECTRODE STATE OF CHARGE ON FILM QUALITY

Coating Quality	Good coverage at longer coating times	Good coverage at longer coating times	Good coverage at longer coating times	Poor coverage initially good coverage on recoating	Good coverage	Good coverage at longer coating times	Incomplete coverage	Incomplete coverage	Incomplete coverage	Incomplete coverage	
Thickness Range mils/side	0.1-2.6	1, 5-2, 5	1.6-7.2	1.6-3.0	1.7-4.8	0.5-3.1	0.4-4.1	1.0-4.0	1.8-3.5	2,0-5,0	
Coating Time Range (minutes)	8-30	8-30	20-50	11-20	13-28	8-30	8-30	8-30	20-50	15-40	
Electrode Numbers	26-29	38-41	1-4	60-64	2-1 to 2-5	34-37	30-33	42-45	5-8	46-49	
Acetate Concentration (grams/liter)	140	140	140	140	140	280	360	140	. 140	360	
Electrode State Pretreatment	Cycled - Discharged - Dried	Cycled - Discharged - Dried	$Cycled$ - $Discharged$ - $Dried^*$	Cycled - Discharged - Dried	Cycled - Discharged - Dried	Cycled - Discharged - Dried	Cycled - Discharged - Dried	Cycled - Charged - Dried	$Cycled$ - $Charged$ - $Dried^*$	Cycled - Charged - Dried	

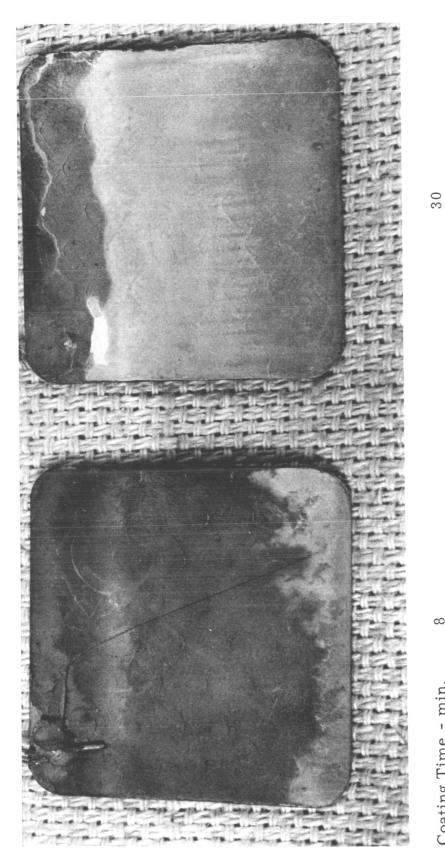
^{*}Mariner Satellite Type Electrodes - Others are all YS5 type.

- 1. The electrodes in the cycled-charged state showed a greater tendency to yield incomplete coatings, compared to the electrodes in the cycled-discharged state. This effect seemed to be more pronounced at the higher electrolyte concentration level of 360 grams per liter than at the 140 grams per liter level.
- 2. For the most complete coatings, the effect of electrolyte concentrations on resistance increase did not appear significant.
- 3. At the longest coating time of 30 minutes, the coulombic efficiency as measured by the weight gains of the films appears to increase with increasing electrolyte concentration from 140 to 280 grams per liter. Increasing the concentration from 280 to 360 grams per liter causes the efficiency to decrease.
- 4. There were no observable effects on film characteristics that could be attributed to the three types of electrodes used.

In the course of this work it was observed that film growth generally proceeded from the bottom edge of the electrode to the top, during the course of a run. The film would become thicker at the bottom edge first, and then with continued coating time the thickness increased progressively to the top edge of the electrode. An increase in agitation of the electrolyte more rapidly removed the evolving hydrogen from the upper portion of the electrode. This, in turn, permitted a more rapid growth of the film to the top edge of the electrode. At the higher electrolyte concentration levels, the increase in solution density and viscosity decreased the degree of agitation provided by the magnetic stirrer at a given setting. From this standpoint it was preferable to use as low a concentration of electrolyte as possible.

The other general problem which influenced film thickness uniformity was the method of making the electrical connection to the electrode. In the early runs an additional electrical lead was spot-welded to the original electrode lead and the electrode was held in place by means of an alligator clip anchored to a rod, with provisions to adjust the elevation of the electrode in the bath. This method generally resulted in a thinner film thickness in the area of the electrode where the original electrical lead was spot-welded to the electrode. After some experimentation the following method was used to minimize this problem. The original electrical lead on the electrode was insulated by spraying a film of Krylon No. 1302. The alligator clip having serrated jaws was insulated with the Krylon film, as well as the rod to which it was attached for positioning in the bath. In this manner electrical paths to the electrodyte were restricted. Electric current flow from the clip to the electrode takes place through the serration tips, which penetrate the electrode.

The improvements in film thickness uniformity obtained with increased agitation and the final method of electrical connection are illustrated in Figures 8 through 10. The preferred range of process variable values and electrode state, and pretreatments for obtaining films of overall good quality in terms of the characteristics evaluated to date, are summarized in Table 4.

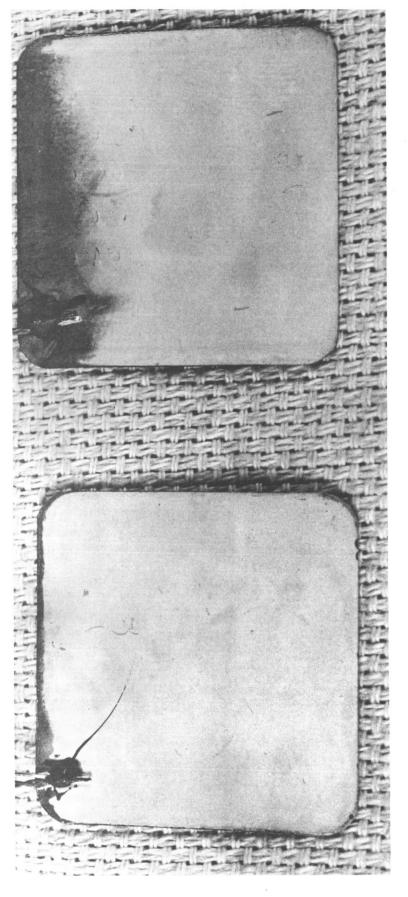


Coating Time - min. 8
Thickness - mils 0.4

Intermediate Level of Electrolyte Agitation Unoptimized Insulation of Electrical Leads

Electrolyte Calcium Acetate - 360 g/1 C.D. - 93 ma/cm²

Effect of Process Variables on Film Thickness Uniformity. Figure 8.

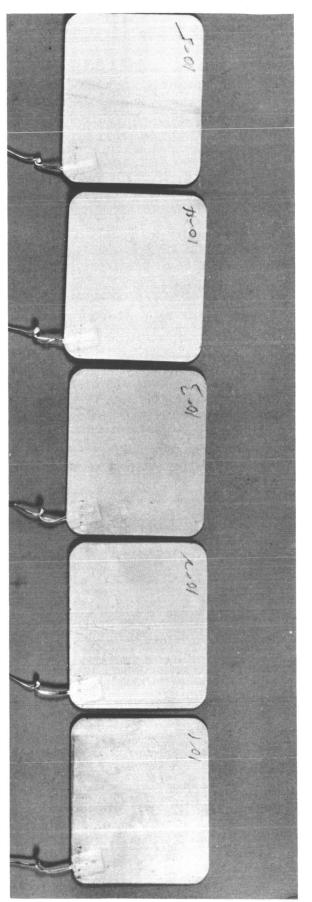


2.5 30 Coating Time - min. Thickness - mils

Intermediate Level of Electrolyte Agitation Unoptimized Insulation of Electrical Leads Electrolyte Calcium Acetate - 140 g/l

 $C.D. - 93 \text{ ma/cm}^2$

Effect of Process Variables on Film Thickness Uniformity. Figure 9.



35	4.7
25	4.5
25	4.5
28	4.1
24	3, 5
Coating Time - min.	Thickness - mils per side

High Level of Electrolyte Agitation Optimized Insulation of Electrical Leads Electrolyte Calcium Acetate - 140 g/1 C.D. 93 ma/cm²

Figure 10. Effect of Process Variables on Film Thickness Uniformity.

Table 4

PREFERRED PROCESS PARAMETER VALUES FOR CALCIUM HYDROXIDE FILMS

Process Parameter	Range
Electrolyte Concentration	70 - 280 grams per liter calcium acetate. Further work is needed to define optimum.
Buffering Concentration	1 - 2 grams per liter calcium hydroxide
Current Density	75 - 155 milliamperes per centimeter squared
Coating Time	10 - 15 minutes for 2 mil thick film
Electrolyte Agitation	Required - improved film coverage and thickness uniformity obtained in shorter time with more intensive rate of stirring.
Electrode State	Cycled-discharged state or cycled-charged state. Improves adherence of film.
Electrode Pore Content	No liquid. Dry in air at elevated temperature 100 - 150°C.

ELECTRODE PERFORMANCE STUDIES

As the electrodes with better films were obtained from the deposition process studies, work on the evaluation of the performance characteristics was conducted in parallel to the process studies.

The principal items investigated are summarized below:

Electrode Capacity under constant current charge-discharge for a small number of cycles (6 to 12) at approximately 100 percent depth of discharge.

Polarization of the electrodes with several film thicknesses over a range of current densities to determine the effective resistance of coated electrodes.

Sterilization of the electrodes in a dry, inert gas environment and in 31 percent by weight potassium hydroxide at 145°C, followed by capacity, polarization, and silver migration determinations.

Silver Migration through the film after short term constant current charge-discharge cycling.

Capacity Results

The capacity tests were made in a test cell, consisting of a single test electrode and two counter cadmium electrodes. One or two layers of nylon separator were wrapped around the test electrode. A plastic, open-mesh screen was placed on each side of the wrapped electrode to provide separation from the cadmium electrode. The test cell components and an assembled cell are shown in Figures 11 and 12. Initially, tests were made without the wrap and the plastic screen. This setup was unsatisfactory, since many of the cells shorted out after a few cycles. This apparently resulted from silver bridging through imperfections in the films.

The electrolyte used was 31 percent by weight potassium hydroxide. Distilled water was added once a day to make up for evaporative losses. The cells were usually cycled from six to twelve times, after a low constant current formation charge and discharge. The charges and discharges were made at constant current. These were varied to some extent, but generally the charge was made at 100 milliamperes. Since the nominal capacity of the various plates in use varied from approximately 1000 to 1250 milliamperehours, the charge rate corresponds to a range of 0.1 to 0.08 C and the discharge rate from 0.2 to 0.16 C. Typical results from these tests are given in Table 5 for electrodes having various pretreatments, and film thickness. These results demonstrate that the capacity developed by the coated electrodes is in the same range as that developed by uncoated electrodes. There is no evidence that capacity is significantly influenced by film thickness.

A comparative capacity test was made with two five-ampere-hour cells-one with electrodes coated to a film thickness of approximately 2 mils per side and the other a control cell with uncoated electrodes. These cells were Yardney Model YS5 containing five silver electrodes and four cadmium electrodes. The original separator system was retained in both cells. The electrolyte supplied by the manufacturer was used. The cells were cycled eight times, the charge rate was 0.3 amperes for 18 hours and the discharge rate was 2.0 amperes. The capacity obtained on the eighth cycle is shown in Figure 13. The voltage time behavior of the two cells, out to 4 ampere-hours, are approximately the same, except for the unexplainable higher starting voltage for the cell with the coated electrodes.

Polarization Results

The potential of the silver electrode versus a mercury-mercuric oxide reference electrode was measured for a number of electrodes in the test cell configuration shown in Figure 12. A condensed tabulation of data for electrodes with varying film thicknesses at discharge currents from open circuit to one ampere (approximately C rate) is shown in Table 6. All of the data points for these electrodes are listed in Appendix V. At 0.1 amperes the polarization of the coated electrodes ranges from 4 to 13 percent less than the average of the uncoated electrodes. At 1.0 ampere—the coated electrode

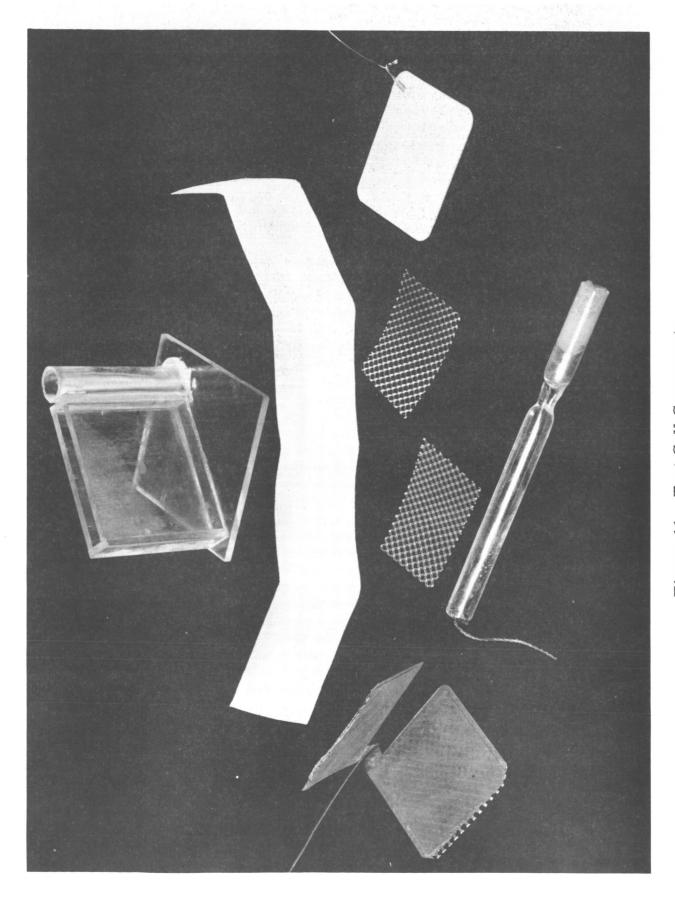


Figure 11. Test Cell Components.

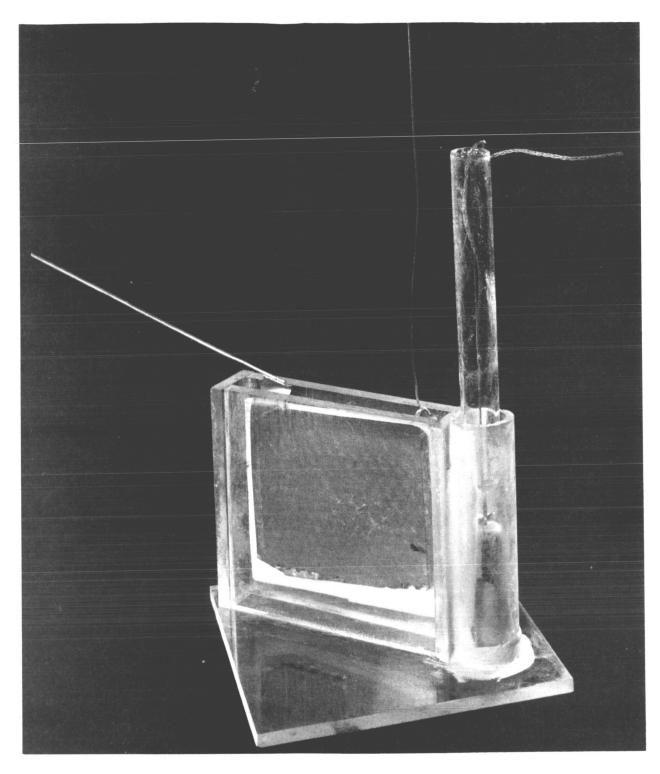


Figure 12. Test Cell Assembly.

Table 5

CAPACITY DATA FOR CALCIUM HYDROXIDE COATED SILVER ELECTRODES

Notes	5th cycle ¹	5th cycle ¹	$egin{array}{c} ext{over} 1 \ ext{5 cycles} \end{array}$	$egin{array}{c} ext{over} \ ext{5} ext{ cycles} \end{array}$	over ¹ 5 cycles	cycles ² 6-9	cycles ¹ 1-9
Capacity ma-hrs	1200	1100	900-1000	875- 975	875- 975	900-1100	960-1175
Resistance 1000 cps ohms	0.260	0.130	0.248	0.182	0.287	0.220	!
Film Thickness mils/side	4.7	1.4	2.6	3.0	1.5	2.1	ı
Coating Conditions	Cycled - Reverse Coated 70 g/1 - 93 ma/cm^2	Cycled - Charged-H ₂ O 70 g/1 - 93 ma/cm ²	Cycled-Discharged-Dried $140~\mathrm{g/l}-93~\mathrm{ma/cm^2}$	Cycled-Discharged-Dried $140~\mathrm{g/1}-93~\mathrm{ma/cm^2}$	Cycled-Discharged-Dried $140~\mathrm{g/1}-93~\mathrm{ma/cm^2}$	Cycled-Discharged-Dried $140~\mathrm{g/1}-93~\mathrm{ma/cm}^2$	Uncoated Electrode
Electrode	20	23	, 29	89	69 35	2-2	ı

1. Formed at charge rate of 50 ma and discharge rate of 100 ma - 2 cycles then charged at 100 ma and discharged at 200 ma. NOTES:

^{- 1} to 5 charge rate increased gradually from 50 to 200 ma. - 6 to 9 charge rate 200 ma and discharge rate 500 ma. Cycles Cycles 8

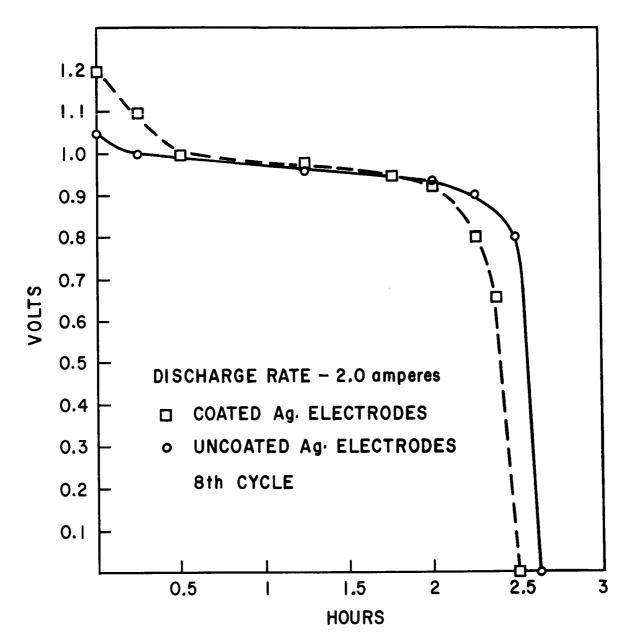


Figure 13. Discharge Voltage Curves - 5 A.H. Cells.

Table 6
POLARIZATION DATA FOR COATED SILVER ELECTRODES

				D i	scha	r g	Rate	- e	a d	r e s				
Film	0	!	0.0		0.0	4	0		0	2	0.	7	1.	
Thickness mils/side	n r	E	E L	ы	Ħ	E C	E L	E	a r	E C	떠	E C	떠님	Б
none	0.244	1.19	0.234	1.18	0.220	1.16	0.210	1.14	0.192	1.11	0.187	1.10		1.07
none	0.243	1.19	0.234	1.17	1	1.16		1.14	0.198	1.11	0.196	1.10		1.08
1.50	0.290	1.19	0.245	1.17	0.215	1.15	0.233	1.13	0.213	1.07	0.210	1.05	0.204	1.10
2.10	0.280	.1.15	0.275	1.14	0.269	1.13	0.250	1.11	0.189	1.00	0.145	0.95	1	}
2.60	0.261	1.19	0.258	1.18	0.244	1.15	0.230	1.13	0.185	1.06	0.170	1.04	0.149	1.00
3.00	0.274	1.20	0.270	1.19	0.253	1.16	0.239	1.14	0.205	1.05	0.197	1.01		0.95
4.75	0,273	1.16	0.269	1.16	0.257	1.13	0.247	1.12	0.211	1.03	0.202	1.00	0.181	0.94
	Film Thickness mils/side none 1.50 2.10 2.60 3.00		Film 0 Thickness mils/side Er Ec none 0.244 1.19 1.50 0.243 1.19 2.10 0.290 1.19 2.60 0.261 1.15 3.00 0.274 1.20 4.75 0.273 1.16	E _r E _c 0.244 1.19 0.243 1.19 0.290 1.19 0.280 1.15 0.261 1.19 0.274 1.20	Cr Ec 0.244 1.19 0.243 1.19 0.290 1.19 0.280 1.15 0.261 1.19 0.274 1.20 0.273 1.16	Cr Ec 0.244 1.19 0.243 1.19 0.290 1.19 0.280 1.15 0.261 1.19 0.274 1.20 0.273 1.16	Cr Ec 0.244 1.19 0.243 1.19 0.290 1.19 0.280 1.15 0.261 1.19 0.274 1.20 0.273 1.16	Cr Ec 0.244 1.19 0.243 1.19 0.290 1.19 0.280 1.15 0.261 1.19 0.274 1.20 0.273 1.16	E _r E _c 0.244 1.19 0.243 1.19 0.290 1.19 0.280 1.15 0.261 1.19 0.274 1.20	Cr Ec 0.244 1.19 0.243 1.19 0.290 1.19 0.280 1.15 0.261 1.19 0.274 1.20 0.273 1.16	Cr Ec 0.244 1.19 0.243 1.19 0.290 1.19 0.280 1.15 0.261 1.19 0.274 1.20 0.273 1.16	Cr Ec 0.244 1.19 0.243 1.19 0.290 1.19 0.280 1.15 0.261 1.19 0.274 1.20 0.273 1.16	E _r E _c 0.244 1.19 0.243 1.19 0.290 1.19 0.280 1.15 0.261 1.19 0.274 1.20	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

 $E_{\rm r}$ - Potential of Ag Electrode Versus Reference Hg/HgO. $E_{\rm c}$ - Potential of Ag Electrode Versus Cadmium Electrode.

ranges from ten percent less to twenty percent greater than the average for the uncoated electrode. The polarization does not appear to be greatly affected by film thickness over the range of 1 to 5 mils per side.

A typical silver electrode polarization curve and total cell voltage curve are shown in Figure 14.

Silver Migration

The effectiveness of the films to control silver migration was determined by analysis of the separator that was wrapped around the coated electrode and in some cases the electrolyte. The analytical procedure is described previously in this section under "Electrode Performance Characteristics." Analysis on the cells was made after the cycling tests to determine the capacity. Results for the various electrodes as compared to uncoated electrodes are shown in Table 7. For the first two groups of electrodes the results are comparable and indicate that the films are effective in retarding silver transport over the course of nine cycles, which was the number these electrodes received. These films, on the Mariner electrodes, were not intact after cycling; they had cracked during the course of assembling the cells. The appearance of the electrodes after cycling are shown in Figure 16. The correspondence of the dark areas of the separator to poorly coated areas, such as the edges and crazed regions is evident by examining Figures 15 and 16. Presumably, the darker areas represent the areas of greatest silver content; however, this was not determined by the analysis of these areas specifically.

The levels of silver transported through the films in the last group of electrodes are somewhat higher than the first two groups. However, the trend still is evident that the coated electrodes are effective in controlling silver migration. The cycling history of the last group of electrodes was different than the first two groups. The latter were cycled at a charge rate of 100 milliamperes and discharged at 200 milliamperes for 8 to 9 cycles. The third group electrodes were charged and discharged at higher rates. For cycles 3 through 5 the charge rate was 200 milliamperes and the discharge rate was 400 milliamperes; for cycles 6 through 9 the charge rate was 200 milliamperes and the discharge rate was 500 milliamperes. Overall, the data suggest that films of two to three mils in thickness may be more effective in controlling silver migration. Additional tests are needed to confirm this trend.

Sterilization Test Results

The preliminary tests, performed early in the program, showed that the coated electrodes could be sterilized without a loss of film. The capacity measurements made on these electrodes generally yielded low (100 to 200 milliampere-hours) to zero capacity after three to six charge-discharge cycles. The electrodes were reverse charged to determine if this would improve the charge acceptance. This treatment did not improve the charge acceptance since capacity values were still low. An examination of the 1000 cycles per

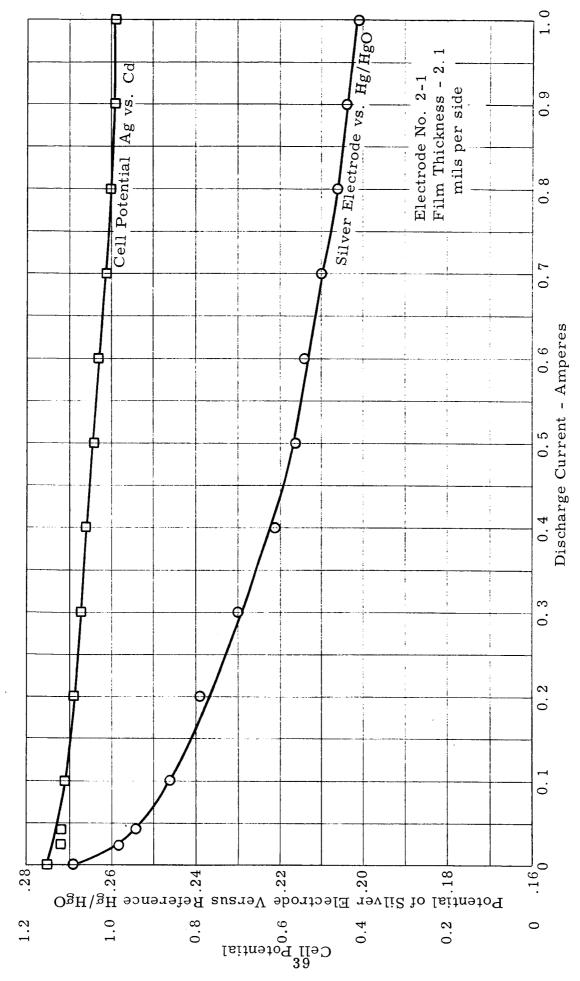


Figure 14. Typical Polarization Curve for Calcium Hydroxide Coated Electrode.

Table 7

COMPARISON OF SILVER TRANSPORTED THROUGH CALCIUM HYDROXIDE FILMS

Notes	Plus 4.0 mg · AgCl in electrolyte ¹	Plus 2.8 mg·AgCl in electrolyte ¹	Electrolyte not analyzed	Electrolyte not analyzed ¹	•	Electrolyte not analyzed 1	;	•	:	6.	Electrolyte not analyzed	Electrolyte not analyzed 2	Electrolyte not analyzed 2
mg of AgCl In Nylon Separator Wrap	4.5	5.2	25.0	31.0		8.0	5, 0	5.0	29.0		12.0	53.0	96.0
Film Thickness mils/side	2.00	3.10	1	1		3,50	4.70	7.20	0.00		2.10	4.75	;
Coating History	Cycled - Discharged - Dried 280 g/l - 93 ma/cm ²	Cycled - Discharged - Dried $280 \text{ g/l} - 93 \text{ ma/cm}^2$	Uncoated	Uncoated	Nectrodes	Cycled - Discharged - Dried $140 \text{ g/l} - 93 \text{ ma/cm}^2$	Cycled - Discharged - Dried $140 \text{ g/l} - 93 \text{ ma/cm}^2$	Cycled - Discharged - Dried $140 \text{ g/l} - 93 \text{ ma/cm}^2$	Uncoated		Cycled - Discharged - Dried $\frac{140 \text{ g/l}}{140 \text{ g/l}} - \frac{93 \text{ ma/cm}}{140 \text{ g/l}}$	Cycled - Discharged - Dried	140 g/1 - 93 ma/cm. Uncoated
Electrode Number	35	37	1	;	Mariner Type Electrodes	2	က	4	1	YS5 - Electrodes	2-2	2-4	S-12

Cycling Conditions - charge rate 100 ma, discharge rate 200 ma. Cycling Conditions - variable - last 4 cycles charge rate 200 ma, discharge rate 500 ma. Notes: 1.

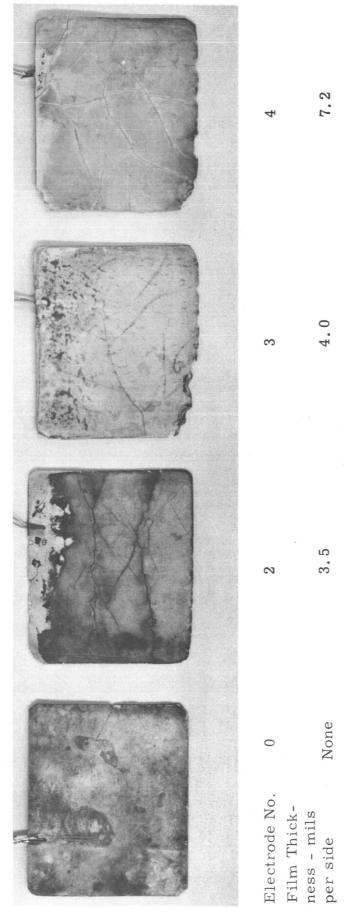


Figure 15. Calcium Hydroxide Coated Electrodes After Cycling Tests. Mariner Satellite Type Electrodes.



 \approx 2 29 Electrode No. AgCl Content Uncoated mg

Nylon Separator Wrapped Around Calcium Hydroxide Coated Electrode After Cycling. Mariner Satellite Type Electrodes. Figure 16.

second resistance values before and after sterilization did not show any major changes that would account for the observed behavior.

The sterilization experiments were repeated with new electrodes with the following modifications in procedure. For the sterilization designated Wet in the following text, the 31 percent by weight potassium hydroxide solution in which the electrodes were immersed was first degassed by boiling for one hour. For the sterilization designated Dry, the electrodes were placed in the Teflon beaker setting in the steel bomb. The assembly was then flushed with dry nitrogen for ten minutes and sealed immediately thereafter. No liquid was used in this case. The purpose of these procedures was to minimize the oxygen content, which might oxidize the electrode or the wire screen grid in the electrode during the course of the sterilization. Using these precautions the coated and uncoated electrodes developed the nominal capacity. The results of these tests are summarized in Table 8. The reason for the low capacity developed by the unsterilized electrode is not known.

A comparison of the effect of sterilization on polarization for coated and uncoated silver electrodes is shown in Table 9 for two current levels. The results indicate there is no adverse effect on the polarization for either coated or uncoated electrodes after sterilization.

The cell resistance calculated from the polarization measurements, expressed in terms of ohms per square inch of electrode cross-sectional area, is tabulated in Table 10. There is no strong correlation with sterilization history, film thickness, or the 1000 cycles per second resistance values.

The migration of silver for two levels of film thickness, with different sterilization history, are compared in Table 11. The data indicate that the thinner films may be more effective in reducing silver migration than the thicker films. In turn thicker firms are more effective than no films at all.

MODIFIED 5 A.H. CELLS

Ten Yardney Model YS5, 5 A.H. silver-cadmium cells were modified and delivered to National Aeronautics and Space Administration Goddard Space Flight Center for testing.

Five cells (numbers 1, 3, 4, 5, and 6) contain silver electrodes with nominal 2 mils per side calcium hydroxide films. Cells numbered 7, 8, 9, 10, and 11 contain silver electrodes with nominal 5 mils per side calcium hydroxide films.

These cells also contain five silver electrodes and four cadmium electrodes. The separator system in these cells is wrapped around the cadmium electrode. This system was left intact and retained in the modified cells. To accommodate the increase in thickness contributed by the films it was necessary to machine the walls of the cell cases. For the cells containing electrodes with the 2 mils per side films, twenty mils were removed from

Table 8

EFFECT OF STERILIZATION ON CAPACITY

		Film	Cap	acity-	MaHr	s.
Electrode Number	Sterilization Type	Thickness mils/side	6 6	YCLE N	UMBER 8	9
S-12	Wet	None	1050	1100	1100	1050
S-7	Dry	1.75	1000	1050	950	1000
2-1	Wet	2.10	1000	1050	1100	1000
2-2	None	2.10	900	1000	1100	950
2-4	None	4.75	500	500	875	625
2-5	Wet	4.75	1050	1000	1100	900

NOTE: Charge rate - 200 ma.

Discharge rate - 500 ma.

Electrodes - Yardney YS5 Type

Table 9
EFFECT OF STERILIZATION ON POLARIZATION

		Film	Disch	arge Ra	te - Ampe	eres
Electrode	Sterilization	Thickness	0.		1.	. 0
_Number	Туре	mils/side	<u>E ref</u>	E cell	E ref	E cell
B-1	None	None	0.210	1.14	0.180	1.07
B-2	None	None	0.210	1.14	0.191	1.08
S-4	Dry	None	0.209	1.17		
S-6	Dry	None	0.209	1.14	0.195	1.07
S-11	Wet	None	0.203	1.11		
S-12	Wet	None	0.246	1.10	0.204	0.99
S-8	Dry	1.75	0.204	1.13	0.175	1.05
S-7	Dry	1.75	0.235	1.10	0.164	0.93
2-1	Wet	2.10	0.246	1.11	0.201	0.99
2-2	None	2.10	0.250	1.11		
2-5	Wet	4.75	0.255	1.10	0.179	0.81
2-4	None	4.75	0.247	1.12	0.181	0.94

Table 10 COMPARISON OF CELL RESISTANCE WITH ELECTRODE FILM THICKNESS AND STERILIZATION HISTORY

			Resistance Polarization	Resistance	
Electrode	Coating	Sterilization	$\frac{\text{x } 10^3 \Omega \text{ / in } ?}{\text{x } 10^3 \Omega \text{ / in } ?}$	1000 cps	Formation
B-1	None	None	13		1
B-2	None	None	26		1
S-4	None	Dry	9	0.120	1
S-6	None	Dry	16	0.075	1
S-11	None	Wet	31	0.100	1
S-12	None	Wet	36	0.100	3
69	1.50	None	16	0.287	2
67	2.60	None	72	0.248	2
68	3.00	None	36	0.182	2
2-4	4.75	None	73	0.520	3
S-8	1.75	Dry	31	0.085	1
S-7	1.75	Dry	71	0.075	3
2-2	2.10	None	145	0.215	3
2-1	2.10	Wet	34	0.285	3
2-5	4.75	Wet	64	0.505	3

Formation History:

- 1 Four cycles charged at 100 discharged 200 2 Five cycles charged at 100 mamp discharged 200 mamp 3 As in capacity studies

Table 11

CYCLED ELECTRODE RESULTS

Observations	Film intact	Film intact	Film intact	Film intact	Film brittle 4 w/% Ag in Film	1
Ag in Separator as mg AgCl	10	26	12	53	84	96
Resistance Polarization x 103 \(\Omega/\)in.	71	34	145	73	64	36
Resistance 1000 cps	0.075	0.285	0.215	0.520	0.505	0.100
Sterilization 1	Dry	Wet	None	None	Wet	Wet
Coating mils/side	1.75	2.10	2.10	4.75	4.75	None
Electrode Number	S-7	2-1	2-2	2-4	2-5	S-12

1. Sterilization was conducted in two ways:

A. In 31% KOH for 40 hours at $145^{\rm O}{\rm C}$ (Wet)

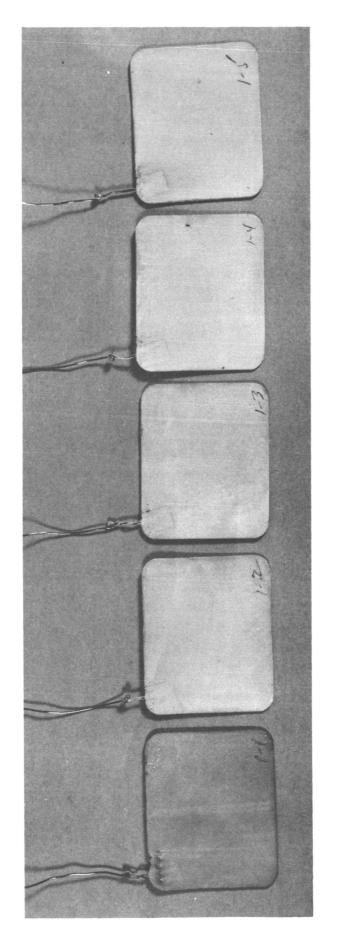
B. In $\rm N_2$ for 40 hours at 145°C (Dry)

one cell wall. For the cells containing the electrodes with thicker films, twenty mils were removed from both cell walls.

The films for these electrodes were deposited from an electrolyte containing 140 grams per liter of calcium acetate buffered with solid calcium hydroxide. The solid hydroxide concentration was initially one gram per liter. Periodic additions of hydroxide were made after every two to three electrodes had been coated. The current density was 93 milliamperes per square centimeter. Prior to coating, the electrodes were cycled once with charging at 200 milliamperes for six hours and discharging at 500 milliamperes for four hours. The electrodes were shorted overnight. Prior to coating, the electrodes were rinsed in distilled water and dried at 145°C for one hour.

The data for the electrodes for each cell are recorded in Appendix VI. The quality of these coatings with respect to coverage and uniformity was good.

The appearance of the electrodes for the two thickness levels is shown in Figures 17 and 18. A view of a partially assembled modified 5 A.H. cell is shown in Figure 19.



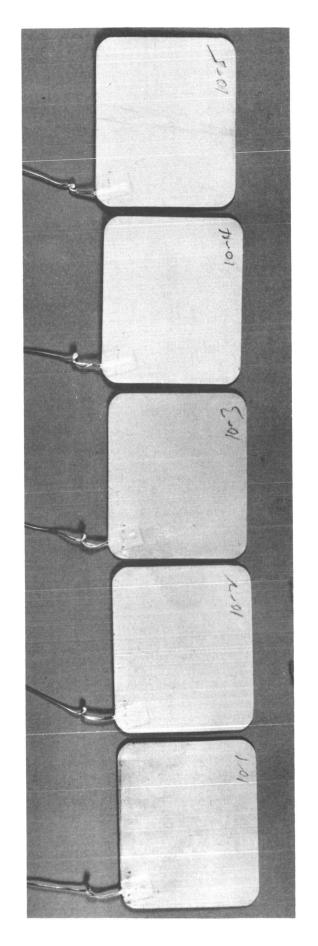
Electrodes Used in Cell Number 1 2.0 1.5 Thickness mils per Actual side

Nominal Film Thickness - 2 mils per Side

2.2

2.2

Figure 17. Calcium Hydroxide Coated Silver Electrodes for Modified 5 A.H. Cells.



4.7 4.5 Electrodes Used in Cell Number 10 4.5 3.5 Thickness mils per side Actual

Figure 18. Calcium Hydroxide Coated Silver Electrodes for Modified 5 A.H. Cells.

Nominal Thickness - 5 mils per Side

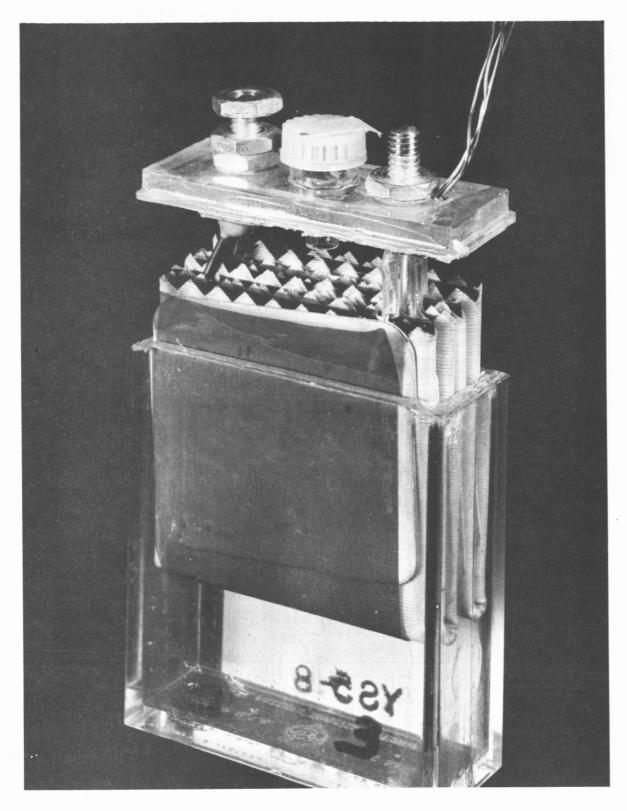


Figure 19. Partially Assembled Modified 5 A.H. Cell.

PRECEDING PAGE BLANK NOT FILMED.

Section 4

NEW TECHNOLOGY STATEMENT

Several areas of new technology were revealed in the course of this study. The areas of significance that are described in this report are referenced below by page number. The areas identified as New Technology are not considered to embrace patent innovations.

- Page 1 -- The first paragraph summarizes the entire program and as such represents new technology.
- Page 3 -- The entire section starting on this page entitled

 Coating Process Description should be considered new technology.
- Page 19 -- Item 1, Adherence and Uniformity of Coverage and Item 2, Other Observations and General Conclusions both represent new technology.
- Page 22 -- Beginning with the third paragraph up to the section entitled Electrolyte Concentration Study Results should be considered as new technology.
- Page 31 -- The data of Table 4 represent a summary of the new technology.
- Page 38 -- The sections entitled Silver Migration and Sterilization Test Results should be considered to be new technology.

APPENDIX I

PRECEDING PAGE BLANK NOT FILMED. Section 5

RECOMMENDATIONS

On the basis of this study, the following recommendations are made.

- 1. Testing of modified 5 A. H. silver-cadmium cells by National Aeronautics and Space Administration Goddard Space Flight Center, should be carried out in order to determine longer term performance capability of coatings with respect to controlling silver migration and and significance of film thickness in performance.
- 2. Assuming the results from the above tests will be encouraging, additional studies should be undertaken to optimize film structure and thickness for use in the silver-cadmium cell system. These studies should include a detailed examination of the film structure, to determine how the film functions in the control of silver migration and transport of hydroxl ions. An additional factor, not examined in the work completed, is the effect of varying the electrode substrate porosity and pore size distribution on the adherence of the film to the electrode and its ability to function as an effective silver migration barrier.
- 3. The value of coating cadmium electrodes should also be examined with respect to obtaining long cyclic life with good cell polarization characteristics. The objective should be to determine what combination of film thicknesses on both electrodes would be equivalent to the presently used organic multi-layer barrier, or if a composite separator system of hydroxide films and organic diffusion barrier would yield optimum performance with lower separator and organic diffusion barrier thicknesses.
- 4. Independent of the above studies, it is recommended that evaluation of these films as separators in the silver-zinc cell system be undertaken. This should have the purpose of controlling both silver migration and zinc dendrite growth.
- 5. Present work on this project has been confined to Laboratory methods of film preparations. Further work on the translation of Laboratory methods to practical controlled processes is required before aerospace cells can be produced satisfactorily.

Appendix I

MAGNESIUM HYDROXIDE FILM DATA

Electrodes -- Silver plates from Yardney YS5-(S)-4 Cells
Uncharged State
Size - 13/16" x 24/16" - one half of original plate size

Electrolyte -- 70 g/l Magnesium Acetate + excess solid ${\rm Mg(OH)}_2$

Sample Number	Current ma.	Time min.	Weight Gain grams	Thickness per side mils	Resistance Gain - 1000cps ohms
1-1	240	60	0.127	2.5	0.035
2-1	240	30	0.091	1.3	0.035
3-1	240	90	0.169	4.3	0.015
4-1	240	120	0.216	6.3	0.005
1-2	488	30	0.129	3.6	0,135
2-2	404	60	0.196	5.7	0.130
3-2	488	90	0.412	12.8	0.110
4-2	404	45	0.168	5.0	0.125
1 - 3	204	30	0.093	0.50	0.055
3-3	204	60	0.139	1.25	0.095
4-3	408	60	0.174	1.75	0.135
1-4	434	120	0.354	5.0	0.055
2-4	430	60	0.176	3.5	0.140
3-4	430	30	0.079	2.5	0.030

Appendix I (continued)

Electrodes -- Silver Plates from Yardney YS5-(S)-4-Cells Uncharged State

MAGNESIUM HYDROXIDE FILM DATA

		ام	÷																								٠			•							
1000 cps esistance :rapolated Values	After	Coating (ohms)								1		0.134	0.142	0.102	0.120	0.120	0.120			0.080	9. 130		0.120	0,107	0.120	0, 120	0.09	0.09			0.102	0.102	0.102	0.102	0.102	0.093	
1000 cps Resistance Extrapolated Values	Before	Coating (ohms)		0.193	0. 193	0.193	0. 193	0.193	0.172	0, 193	0. 193	0, 193	0. 193	0. 193	0.193	1	ı			0. 200	0.230		0 132	0.132	0, 132	0.132	0.120	0.120			0.230	0.150	0.212	0.172	0.180	0.173	
	Thickness of Film	per Side (mils)		0.3	0.15	0.1	0.05	0.05	0	0.25	0.4	9.0	0.35	0.00	0.85	2	1			2.85	2.1		4	0.25			0.2	3, 75	:		0.8	6.0	1.5	9.0	3.7	5.8	
	Weight	Gain (grams)		0.084	0.091	0,081	0.099	0.106	080.0	0.010	0.054	0.016	0.015	0.005	0	038	054			0.128	0.161		001	0.100	0 233	0.255	0.099	0.216			0.317	0.228	0,326	0.343	0.474	0.764	
	Final	Voltage (volts)		2.83	2.5	2.08	2.22	2.32	2.28	3.85	3.46	3.45	3,34	4.25	4.24	4.25	4.3			3.32	4.3		c	2.00		2.8	2.65	3 03	20.0		4.12	4.1	4, 92	4.9			
te	Initial	Voltage (volts)		1.6	1.9	1.75	1.7	1.7	1.6	3.3	2.75	2.8	2.6	3.0	3.1	3.95	4			2.1	3.8		ď	7) (7 0	* · ·	۳	7 0	٠. ۲		3.6	6	4	4		•	
ed Sta		Time (min)		30	30	30	9	90	90	30	120	9	9	06	09	9	09			150	09		ć	2 5	000	000	0 4	3	00		9	90	90	9	y on v	ין מיניט סמוע	e omy
Uncharged State		Current (ma)		122	122	61	61	61	61	488	488	244	244	488	488	244	244			244	488	rt.	•	122	122	488	400	777	488		488	188	400	916	200 310 4 dinned in acetate only	dum accea	dipped in acetate only
Þ	Current	Density (ma/in ²)	size	90	50	25	25	25	25	200	200	100	100	200	200	100	100			100	200	*C-OC prior to coat		20	90	200	200	000	200		100	100	007	200	4. 4:55	* dipp	ddip *
	Hydrovide	Concentrations (g/1)	late	. 1		, ,		•	1			•			_					*	1	*C-OC		1		•	1	•	ı	al plate size	-	- -	-	- 1 ,	7	١.	
	Acctoto	Concentrations	x 24/16" -	02	2 2		20 €								. ×		07 ~ 30		*=rerun	~ 450				~ 140	~ 140	~ 140	~ 140	~ 450	~ 450	$x 1 1/2^{n}$ - original plate			~ 450			~ 450	~ 450
		Sample No	9			10/10 2									10/19 5*		10/19 17	1	I=#	11/11	11/11 2			10/28 1		10/28 3		10/28 5	10/28 6	Size - 1 5/8"				11/4 3			11/4 6

APPENDIX II

Appendix II
CALCIUM HYDROXIDE FILM DATA

Electrodes -- Silver Plates from Yardney YS5-(S)-4 Cells Uncharged State

Electrolyte -- 70 g/l of Calcium Acetate + excess solid Ca(OH)₂

Sample Number	Current ma.	Time min.	Weight Gain grams	Thickness per side mils	Resistance Gain - 1000 cps ohms
Size - 13/16" x 3	24/16" o	ne-half c	riginal pla	te size	
1-1	210	60	0.021		
plus	420	60	0.400		0.06
2-1	420	120	0.098		0.045
3-1	750	165	0.176	1.0	0.89
4-1	750	165	0.175	0.95	0.55
1-2	800	30	0.166	1.5	0.19
2-2	800	60		15	0.31
plus	500	135		2.0	0.51
Size - 1-1/2" x	1-5/8'' c	riginal p	late size		
1-1 plus	500 1000	120 60	0.322 0.350		
			0. 672	25	0., 53
2-1	1000	60	0.404	2.5	0.71
3-1 plus	1000 1000	45 45	0.473	2 .5	0.77
1-2	1000	60	0.614	2.5	0.60
2-2	1000	45	0.396	2.0	0.50
3-2	1000	45	0.390	2.0	0.42
4-2	1000	45	0.341	1.0	0.53
1-3	1000	45	0.540	2.5	0.17
2-3	1000	45	0.485	2.2	0.29
3-3	1000	45	0.364	1.1	0.17
ectrode charge	d @ 100 ma	for 16 h	rs. prior	to coating	
1	1000	60	0.303	3.5	0.21
2	1000	60	0.431	7.5	0.36

Appendix II (continued)

CALCIUM HYDROXIDE FILM DATA

Electrodes -- Silver plates from Yardney YS5-(S)-4 Cells Uncharged State Size - 13/16" x 24/16" - one-half of original plate size

												. •	•					·					•												
cps	olated	After	Coating	(swuo)	0.210	0.210	0.210	0.210	0.122	0.112	0.142	0.162	0.170	0.110	0.110	0.100	0.100	0.110	0.170	0.190	0.210	0.290	0.262	0.190	0.170	0.150	0.210	0.180	0.210	0.250	0.280	0.210	0.250	0.260	
1000 cps Resistance	Extrapolated	Before	Coating	(smrlo)	0.092	0.105	0.085	0.105	0.088	0.088	0.088	0. 088	080	060 '0	0.080	0.080	0.072	0.080	0.080	0.080	0.183	0.170	C. 170	0.170	0.170	0.183	0.170	0.193	0.170	0.208	0.175	0.198	0.172	0.172	
size	Thicket	of Film	per Side	(mils)	0.05	0.05	0.4	6`0	0	0	2.8	1.9	1.6	1.75	0	0	2.3	2.2	2.3	က		2.2	3.3		1.3	1.35	1.15	1.05	2.55	2.1	2.6	3, 55	1.75	2.0	
one-half of original plate	ı	Weight	Gain	(grains)	0.005	900.0	0.054	0.096	0.013	0.010	0.306	0.272	0.155	0.217	0.065	0.067	0.354	0.330	0.382	0.409	0.223	0, 227	0.279	0.341		0.170	0.151	0.123	0.252	0.252	0.290	0.337	0. 206	0.215	
f of origi	•	Final	Voltage	(volts)	5.8	6.3	7.8	8.4	13	9.6	46.	39	20	50	8.4	8.6	18.6	16.3	46	47.5	23	21	40	42	8.9	9.05	19.6	16.8	31.5	24.5	42	22.5	11	14	
one-hali		Initial	Voltage	(volts)	•		3.2	3.1	3.3	3.2	3.4	3.45	4.7	3,9	3.9	3.9	4.1	3.9	4. 1	3.9		5.7		4.8	5.4	5.1	7.5	6.9	7.4	7.1	7.4	6.8	5.1	5.2	
1			Time	(mim)	30	30	45	45	9	09	06	90	45	40	15	15	30	30	45	35	15	15	25	28	10	10	5	5	10	10	13	15	15	15	
arged State - 13/16" x 24/16"			Current	(ma)	488	488	488	488	488	488	488	488	976	946	916	946	916	946	916	916	1465	1465	1465	1465	1465	1465	2440	2440	2440	2440	2440	2440	1465	1465	
Uncharged State Size - 13/16" x		Current	Density	(ma/ın-)	200	-200	200	200	200	200	200	200	400	400	400	400	400	400	400	400	009	900	009	009	009	009	1000	1000	1000	1000	1000	1000	900	009	
Ur.		Hydroxide	Concentrations	(g/1)	•	,			•	1	ı	1	1	•		•		•		1	-	•	-	•		1	1	-	•		•	1		ı	
		Acetate	Concentrations	(g/1)	20	70	7.0	70	70	70	20	70	70	70	70	70	70	70	70	70	70	70	70	70	70	7.0	70	70	20	20	70	0.2	02	20	
			;	No.	1	7	က	4	2	9	7	ω	-	7	က	4	5	9	7	&	-	2	က	4	သ	9	-	2	e	4	Ŋ	9	-	7 2	ı
			,	Sample No.	9/17	9/17	9/17	9/17	9/17	9/17	9/17	9/17	9/21	9/21	9/21	9/21	9/21	9/21	9/21	9/21	10/4	10/4	10/4	10/4	10/4	10/4	10/11	10/11	10/11	10/11	10/11	10/11	10/18	10/18	1 - 1



PRECEDING PAGE BLANK NOT FILMER Prendix III

CALCIUM HYDROXIDE FILM DATA

1

Electrode-State and Pretreatment Uncharged-KOH Reverse Coating for 10 min. H20 Dried - 145°C Eycled-Discharged-KOH H20 Dried - 145°C Reverse Coating for 20	No. Elec. 3 4 4 8 12 12 15 16 10 11 11 13 2 2 2 2 2 2 2 2 2 2 3 6 19 17 *	Initial Weight Grams 6.277 6.883 6.900 6.622 7.197 6.885 6.610 6.656 6.877 6.674 6.694 6.599 6.762 6.852	Initial Thickness mils 28.5 28.3 28.8 28.5 28.7 28.7 28.5 28.6 28.6 28.6 28.6 28.6 28.6 28.6 28.6	Resistance ohms Initial Finitial Finiti	nce s Final 0.080 0.043 .101 .062 .112 .083 .112 .088 .110 .090 0.090 0.061 .119 .060	Coating Time Min. 15 20 20 20 20 20 20 20 20 20 20 20 20 20	Initial Volts 6.6 5.8 6.4 6.4 5.9 5.7 6.4 5.7 6.4 5.0 6.4 6.4 6.4 6.4 5.0	Final Volts 24 34 42.8 34 42.8 42.8 42.8 42.8 42.8 42.8 42.8 42.	Weight Gain Grams O73 O68 O73 O68 O43 O45 105 106 107 107 107 107 107 107 107	Film Thickness mils/side 0.05 0.05 0.05 0.05 0.05 0.05 0.05 0.0
Charged-H ₂ O Dried - 145°C	23 24 14 18 25	6.656 6.672 6.655 6.738 6.413	28.6 28.1 28.5 28.5 28.5	.140 .130 .120 .170	.130 .300 .070 .175	20 20 20 20	6.4 % % % % % % % % % % % % % % % % % % %	42.9 42.9 42.6 42.9 42.8	.480 .718 +.295 .304	1.4 3.0 *1.75 1.25 2.0
•	•	,								

*Coated in a fresh volume of electrolyte after reversal. Electrolyte Concentration - 70 g/l Full Size Electrodes - 1-5/8" x 1-1/2"

NOTES:

APPENDIX IV

ELECTROLYTE CONCENTRATION STUDY DATA

											•			A	ър	рe	en	di	x	IV	7																					
ed G	After	Coating (ohms)	0.112	0.120	0.040	0.083	0.092	0, 141	0, 130	0.080	0.160	0.210	0.470	0.450	0.635	0.330	0.360	0.276	0.318	0.448	0.456	0, 560	0.180	0.580	0.200	0, 495	0.300	ا	0.248	0.182	0.30	0.22	0.51	_	0, 13	0, 10	0.10 *	* 80 .0	* * 60.0	* *	0.10 *	0.10 *
Extrapolated Values	Before	(ohms)	0.070	0.070	0.080	0.070	0.078	0.070	0.070	0.044	0.044	0.062	0.343	0.370	0.280	0, 150	0, 120	0.190	0.180	0.215	0.161	0.380	0, 367	0.330	0,070	0.070	0.070		1ead 0.092	0.092	0.10	0.10	0.10	0.13	0.07	0.11	0.10	0, 10	0.10	0.00 0.10	0.10	0.10
Thickness	of Film	per side (mils)	2.2	0.1	; o .	4.4	0.5	2.0	2, 2, 2, 2, 4, 4, 4, 4, 4, 4, 4, 4, 4, 4, 4, 4, 4,		1.5	1,6	0.1	2.5	0.4	2.5		 	3.5	4.7	2.	2.7	2,8		2.5	2.6	6.1		. 2. 4. 6. 4	3.0	1.7	2.1	• • •	1.8	2,0	2.0	• •	,	•		•	1
	Weight	(grams)	0.217	0.161	0.193	0.401	0.193	0.407	0,567	0	0,153	0,178	:	• •	ı		•			·			,	1 0		0.525	0.444		0,571	0.675	0.410	0.500	0,961	0.317	0.378	0.292		•	4		,	ı
	Coating	(min)	8 15	50	, w .	50 5	, w	15	30	, c	15	30	, co	15	30	20	30	° 50 80 80 80 80 80 80 80 80 80 80 80 80 80	30	40	20	0 0 8	9	20	15	12	11	broke	12	17	13	14	28	12	12	12	• •			, ,	,	•
	Initial	(mils)	28.7	28.7	28.7	4 6 4 6	28.6	28.6	28.9	23.1	23.1	23.1	22.9	23.2	23.2	23.1	23.0	20.0	20.6	20.4	20.7	21.0	20.5	20.4	24.0	23.8	24.0	lead	8 8 8	.23.2	23.0	22.6	22. 7	22.5	22.9	23.0	23.0	23.0	22.8	23.0	23.0	22.6
	Initial	weignt (grams)	6.790	6.713 8.890	6.712	6.651	6.801	6, 667	6, 767	4, 865	4, 832	4.880	4. 764	4,830	4.854	4.846	4, 780	4. 936	4.261	4, 165	4.100	4,045	4.081	4.324	4. 760	4.770	4, 833	lost	4.822	4, 638	4.734	4. 704	4,645	4.834	4.697	4.886	4.812	4.833	4,814	4, 827	4,851	4.737
	- 10	Number	29	32 6	30.5	32	34	35	36	38	39	40	42	44	. 4)	47	48	[49 (1	83	<u>~</u>	* ;	. u	· ·	80 (61	\$25* 	64*	(65	67	88	(89 (2-1	2-2	2 2 4	 -s 	S-8	S-14	S-3	S-5	8-e	S-9	S-11	(S-12
	Acetate	Concentration g/1		140	Coc	0000		280			140		•	140			360		140	2			140		•	140			140				140				•,					
	Electrode State,	Pretreatment and Comments	Cycled-Discharged-Dried	Good Coverage at Longer Coating Time	Cycled-Discharged-Dried	incomplete coverage	Cycled-Discharged-Dried	Good Coverage at: Longer Coating Time		Cycled-Discharged-Dried	Good Coverage at Longer Coating Time	•	Cycled-Charged-Dried	Incomplete Coverage	; ;	Cycled - Charged - Dried Incomplete Coverage		Cycled-Discharged-Dried	Mariner Type Electrode	Good Coverage at Longer Coating Time		Cycled-Charged-Dried Mariner Tune Electrode	Incomplete Coverage		Cycled-Discharged-Dried * Initially Poor Coverage	Recorded-Good Coverage		Cycled-Discharged-Dried	Good Coverage		Cycled-Discharged-Dried	Good Coverage					Uncoated-Dry Sterilization	Wild Stell Lieation	; ;	Uncoated-wet Stermization * After Sterilization		

APPENDIX V

ELECTRODE POLARIZATION AND CELL POTENTIAL DATA

_	ē.	2	Ec	1.19	1.17	1.17	1.15	1.13	1.11	1.10			1.09			1.07	1.06	1.05	1.04	1.02	1.00
69	none	1.5	r Er	0.270	0.263	0.257	0.245	0,233	0.221	0.215			0.215			0,213	0, 211	0.210	0.208	0.205	0.204
89	none	3.0	Ec	1.20	1, 19	1.18	1,16	1.14	1.11	1.08			1.06			1.05	1.03	1.01	1.00	0.97	0.95
g	. 5	က	되	0.274	0.270	0.264	0,253	0.239	0,225	0,219			0, 212			0,205	0.200	0.197	0.194	0,190	0.188
	o		Ec	1.19	1.18	1.17	1, 15	1.13	1.11	1.11			1.09			1.06	1.05	1.04	1,03	1,01	1.00
67	none	2.6	ā	0.261	0.258	0.254	0.244	0.230	0,208	0.200			0.192			0,185	0.176	0.170	0.163	0.156	0.149
4		ø.	Ec	1.10	1.10	1.11	1.11		1.10		1.09			1.08							
S-11	wet	none	<u>;</u>	0.204	0.205	0,205	0.204		0.201		0.200			0.197							
		ις	Ec	1.17	1.15	1,15	1.14	1.13	1.12	1.11			1.10			1.09	1.08	1.07	j. 07	1.06	1.05
S-8	dry	1.75	Er.	0.240	0.220	0,216	0.210	0.204	0.199	0.195			0.193			0.190	0.187	0.184	0, 181	0.178	0.175
			Ec	1.18	1.16	1,15	1.15	1.14	1.12	1.12			1.11			1.10	1.10	1.09	1.08	1.07	1.07
S-6	dry	none	Er	0.237	0.223 1	0.218	0.214 1	0.209	0.207	0.205 1			0.203 1			0.201	0.200	0.199	0.197	0,196	0.195 1
		0)	Ec	1.17	1.19	1.18		1.17	1.15			1.14			1.12						
S-4	dry	none	E	0.211 1	210 1	. 210 1		0,209 1	0,206 1			. 204 1			, 203 1						
			Ec	0 61.1	1.17 0	1.17 0	1.16	1.14 0	1.13 0	1.12		0	1.12		0	1.11	1.11	1, 10	1.09	1,09	1.08
B-2	none	none	Er	0.243 1	0.234 1	0.225 1	0.220	0.210 1	0.203 1	0.200 1			0.199 1			0.498	0.197	0,196	0.194 1	0.193 1	0.191
,			-33																		
B-1	none	none	* Ec*	4 1.19	4 1.18	6 1.17	0 1.16	0 1.14	3 1.13	8 1.12	٠		5 1.12			2 1.11	0 1.10	7 1.10	4 1.09	3 1.09	0 1.07
	_	-	Er	0.244	0.234	0.226	0.220	0.210	0,203	0.198			0.195			0.192	0.190	0.187	0.184	0.183	0.180
Electrode Number	Sterilization	Film Thickness (mils/side)	Current (milliampere)	0	10	20	40	100	200	300	320	350	400	445	450	500	009	7007	800	006	1000

*Er = Ag electrode potential versus Hg/HgO reference electrode. *Ec = Cell potential.

Appendix V (continued)

Electrode Number	2	2 - 1	2-2	5	2-4	4	2-5	છ	S	Z-Z	Ś	S-12
Sterilization	*	wet	none	ue ue	none	ne	wet	et.	Ġ	dry	M	wet
Film Thickness (mils/side)	23	2.1	2	2.1	4.75	75	4.75	22	ij	1.75	ou	none
Current (milliamperes)	Er*	된 *	Er	臣C	Er	Ec	Er	Ec	Er	<u>ਬ</u>	Er	Ec
0	0.269	1.15	0.280	1.15	0.273	1.16	0.284	1.15	0.264	1.14	0.270	1.14
10	0.262	1.14	0.275	1.14	0.269	1.16	0.279	1.14	0.261	1.14	0.265	1.12
20	0.258	1.12	0.270	1.14	0.265	1.15	0.273	1.13	0.254	1.13	0,260	1.12
40	0.254	1.12	0.264	1.13	0.257	1.13	0.267	1.12	0.245	1.11	0.255	1.11
100	0.246	1.11	0,250	1,11	0.247	1.12	0.255	1.10	0.235	1.10	0.246	1.10
200	0.239	1.09	0.228	1,09	0.235	1.10	0.238	1.08	0.223	1.08	0.235	1.09
300	0.230	1.07	0.206	1.05	0.225	1.08	0.224	1.05	0.214	1.06	0.229	1.07
400	0.221	1,06	0.189	1,02	0.217	1.06	0.219	1.02	0,206	1.04	0.224	1.06
200	0.216	1.04	0.174	1.00	0.211	1.03	0,211	0,99	0.200	1.03	0.220	1.05
009	0.214	1.03	0.159	0.97	0.207	1.01	0,203	96.0	0.192	1.01	0.215	1.04
700	0.210	1.01	0.145	0.95	0.202	1.00	0.194	0,93	0,185	1.00	0.211	1.02
800	0.206	1.00	0.133	0.92	0.192	96.0	0.189	06.0	0.178	0.97	0.211	1.01
006	0.204	0.99			0.187	96.0	0.184	0.86	0.170	0.95	0.206	1,00
1000	0.201	0.99			0.181	0.94	0.179	0.81	0.164	0.93	0.204	0.99

 $*\mathrm{Er}$ = Ag electrode potential versus Hg/HgO reference electrode $*\mathrm{Ec}$ = Cell potential

APPENDIX VI

Appendix VI DATA FOR ELECTRODES USED IN MODIFIED YS-5 A.H. CELLS

YS-5 Modified Cell Number	Electrode Number	Initial Weight (grams)	Initial Thickness (mils)	Initial Resistance (ohms)	Final Resistance (ohms)	Coating Time (min)	Initial Volts	Final Volts	Weight Gain (grams)	Film Thickness (mils/side)
1	1-1	4.797	23. 0	0.09	0.19	12	5.5	16.4	0, 294	1.5
	1-2	4.796	23. 0	0.11	0.20	12	5.2	14.0	0, 347	2.0
	1-3	4.789	23. 0	0.10	0.21	14	5.2	11.8	0, 377	2.2
	1-4	4.782	23. 0	0.10	0.21	13	5.0	10.6	0, 385	2.2
	1-5	4.791	22. 7	0.09	0.21	14	5.0	10.8	0, 401	2.2
3	3-1	4.832	23.2	0.08	0.08	13	5.7	17.0	0.287	1.9
	3-2	4.830	23.0	0.08	0.11	12	5.3	14.0	0.303	2.0
	3-3	4.833	23.1	0.08	0.15	12	5.2	16.0	0.400	2.5
	3-4	4.800	23.0	0.08	0.15	12	5.1	16.0	0.436	2.5
	3-5	4.818	22.9	0.08	0.20	12	5.0	15.5	0.450	2.5
4	4-1	4.769	22.6	0.10	0.11	10	5.5	18.0	0, 216	1, 2
	4-2	4.789	22.6	0.10	0.11	12	5.5	16.8	0, 315	1, 7
	4-3	4.829	23.2	0.10	0.20	12	5.2	17.0	0, 381	2, 3
	4-4	4.886	23.0	0.10	0.16	13	5.0	15.2	0, 411	2, 3
	4-5	4.792	23.2	0.10	0.22	13	5.1	14.6	0, 430	2, 4
5	5-1	4.889	23.4	0.06	0.15	12	5.6	19.0	0.303	1.8
	5-2	4.697	23.0	0.06	0.21	13	5.2	13.8	0.503	2.4
	5-3	4.761	22.6	0.06	0.35	12	5.6	16.2	0.495	3.0
	5-4	4.758	23.4	0.06	0.28	13	5.4	14.0	0.492	2.8
	5-5	4.659	22.8	0.06	0.32	13	5.3	14.2	0.513	3.1
6	6-1	4.843	23.0	0.08	0.09	15	5.8	13.3	0.188	1.3
	6-2	4.810	23.0	0.05	0.13	13	5.6	13.8	0.336	2.0
	6-3	4.702	23.0	0.08	0.20	12	5.2	14.6	0.399	2.2
	6-4	4.802	22.8	0.08	0.17	12	5.3	18.0	0.325	2.1
	6-5	4.699	23.0	0.10	0.28	10	5.0	9.8	0.468	2.5
7 .	7-1	4. 737	22.5	0.04	0.35	30	5.8	42.3	0.589	5.3
	7-2	4. 860	23.0	0.05	0.50	25	4.0	42.3	0.841	6.0
	7-3	4. 743	23.0	0.06	0.47	20	4.0	42.3	0.744	5.5
	7-4	4. 729	23.0	0.05	0.36	23	4.1	42.0	0.663	6.5
	7-5	4. 748	23.0	0.06	0.50	28	3.6	42.2	0.709	5.0
8 .	8-1	4.608	22.6	0.04	0.12	29	4.8	42.2	0.349	3.5
	8-2	4.689	23.0	0.03	0.30	29	5.0	42.3	0.651	4.2
	8-3	4.683	22.8	0.06	0.32	30	4.5	42.0	0.675	3.9
	8-4	4.623	22.8	0.06	0.47	22	4.6	42.2	0.732	4.3
	8-5	4.681	22.9	0.04	0.49	27	3.7	42.3	0.857	4.6
9	9-1 9-2 9-3 9-4 9-5	4.747 4.756 4.738 4.743 4.754	23. 0 23. 3 23. 2 23. 3 22. 8	0.10 0.08 0.11 0.04 0.04	0.51 0.53 0.66 0.59 0.52	25 25 20 27 30	5.8 5.1 4.7 4.8 4.4	42.3 42.0 42.3 42.3	0.627 0.788 0.857 0.896 0.994	4. 0 4. 7 5. 0 5. 2 5. 7
10	10-1	4.720	23. 0	0.06	0.27	24	6.0	42.2	0.474	3.5
	10-2	4.796	23. 0	0.05	0.33	28	5.1	42.0	0.721	4.1
	10-3	4.794	23. 0	0.07	0.59	25	4.7	42.3	0.729	4.5
	10-4	4.737	23. 0	0.04	0.48	25	5.6	42.3	0.779	4.5
	10-5	4.824	23. 2	0.07	0.60	35	4.8	42.0	0.884	4.7
11	11-1	4.685	23. 0	0.09	0.34	28	5.0	42.3	0.534	4. 2
	11-2	4.643	23. 0	0.11	0.34	30	3.8	42.3	0.687	5. 5
	11-3	4.639	22. 9	0.09	0.55	30	4.6	42.3	0.810	5. 0
	11-4	4.613	22. 8	0.11	0.45	33	4.7	42.2	0.737	4. 9
	11-5	4.694	23. 0	0.12	0.50	32	4.6	42.3	0.736	4. 6

*Electrolyte -- 140 g/l calcium acetate
 ~ 1 g/l calcium hydroxide
 Current density = 93 ma/cm²
 Electrode state--cycled, discharged, and dried